Assignment of structure **1** to vpc peak no. 4 was made on the basis of the following evidence (a) the ir spectrum of **1** (mixed with **3**) showed no absorptions inconsistent with the proposed structure; (b) when **1** (mixed with 35% **3**) was heated in a sealed tube for 4 days (temp 100°), it largely rearranged to a mixture of **2**, **3**, and **4** (we confirmed that significant net loss of isomers did not occur by including *p*-chlorobromobenzene in the mixture as an internal standard); and (c) the nmr spectrum is consistent with this structure. As stated above, the spectrum showed four regions of absorptions (60 MHz, δ 2.71, 4.45, 4.89, 5.99) with integrated intensities of 2:1:1:2, respectively. Decoupling experiments (Varian XL-100) showed that the multiplet at δ 4.45 collapsed to a doublet when the protons centered at 2.71 were irradiated. Irradiation of the proton centered at δ 4.89 caused the multiplet at 4.45 to collapse to a triplet. The broad doublet at δ 2.71 collapsed to a broad singlet when the proton at 4.45 was irradiated. Unlike the trans-3,4 isomer, **2**, the methylene hydrogens in **1** apparently have the same chemical shift and do not couple with each other.

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Reference and Notes

(1) Cis-1,2 addition of chlorine has been observed with phenanthrene [P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger, *J. Chem. Soc.*, 5285 (1961)] and acenaphthalene [S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *J. Amer. Chem. Soc.*, **78**, 4939 (1956)] and has been suspected in the cases of 1-phenylpropene [R. C. Fahey and C. Schubert, *ibid.*, **87**, 5172 (1965)] and stilbene [S. J. Cristol and R. S. Bly, *ibid.*, **82**, 142 (1960)]. In these four olefins the double bond is in conjugation with an aromatic ring.

(2) *cis*-1,2-Dichlorocyclopentane was synthesized according to the procedure that N. Isaacs and D. Kirkpatrick [Tetrahedron Lett., 3869 (1972)] used for the preparation of *cis*-1,2-chlorocyclohexane.

(3) F. Tailly, *Bull. Soc. Chem. Fr.*, 38 (1962).

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(5) It is conceivable that the structural assignments in the previous studies[3,4] were correct, but that the assignments were made on thermodynamic rather than kinetic products. We have found that the thermodynamic dichloride mixture (formed by heating a dichloride mixture) consists of predominately 3,5-dichlorides. In the previous studies the dichloride products were distilled without regard for rearrangement.

(6) A detailed analysis of the nmr spectra of the dibromides corresponding to dichlorides **2**, **3**, and **4** has recently been published in this journal [G. E. Heasley, V. L. Heasley, S. L. Manatt, H. A. Day, R. V. Hodges, P. A. Kroon, D. A. Redfield, T. L. Rold, and D. E. Williamson, *J. Org. Chem.*, **38**, 4109 (1973)].

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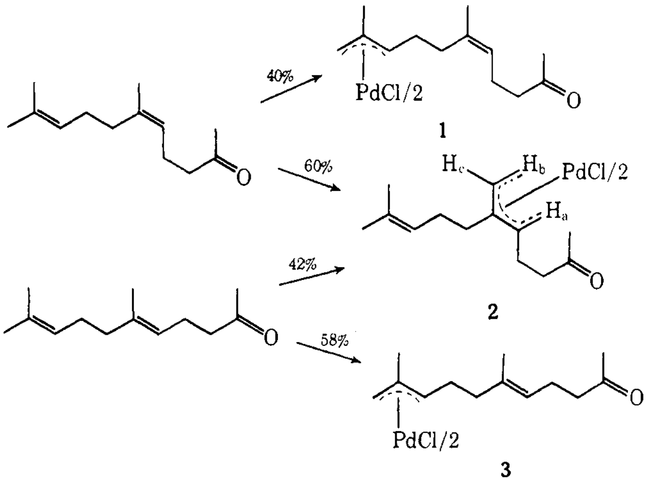
New Synthetic Reactions. Chemospecificity of Allylic Alkylation

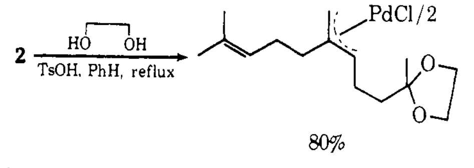
Summary: Selective alkylation of the methyl groups of geranylacetone without protection of the carbonyl group has been aschieved *via* the intermediacy of π-allylpalladium complexes.

Sir: The activation of the α position of carbonyl compounds for formation of carbon-carbon bonds contributes to the importance of the carbonyl group in organic synthesis. The double bond has not generally served such a role.[1] One approach to this problem involves alkylations utilizing π-allylpalladium complexes as intermediates which, in turn, are generated from the olefins.[2] We wish to report that this method allows selective alkylation α to the double bond even in the presence of a carbonyl group.

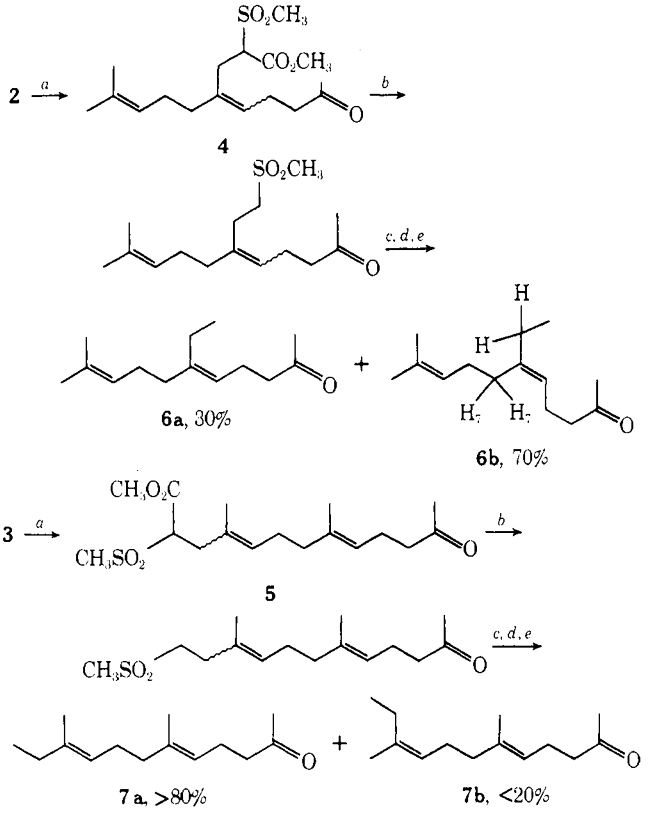
Treatment of *cis*- or *trans*-geranylacetone with palladium chloride, sodium chloride, cupric chloride, and sodium acetate in acetic acid proceeds regiospecifically to produce the π-allylpalladium chloride dimers **1** and **2** (from cis) and **2** and **3** (from trans) in 70-85% yields.[3,4] The isomers are easily separated by preparative tlc and characterized by their nmr spectra. Isomers **1** and **3** are distinguished from **2** by the presence of the methyl group on the π-allyl unit at δ 2.12 and 2.10, respectively.[5] They are distinguished from each other by the downfield chemical shift of the vinyl methyl group of **1** (δ 1.70) compared to **3** (1.65).[6] It should be noted that the geometry of the double bond of these products completely reflects that of starting material. However, reaction at the central double bond leads to the same π-allylpalladium chloride dimer from either *cis*- or *trans*-geranylacetone.[3] The syn stereochemistry of **2** is assigned on the basis of comparing nmr spectral characteristics (δ_{Ha} 3.40, δ_{Hb} 2.70, and δ_{Hc} 3.63) to related complexes of known stereochemistry.[3,5] Recovered geranylacetone from these preparations shows no loss of double-bond geometry.



The remarkably stability of these complexes is illustrated by the ability to ketalize the carbonyl group without decomposition under normal conditions. On the other hand, such protection was unnecessary for subsequent alkylation. Treatment of either **2** or **3** with the anion of methyl methylsulfonylacetate in the presence of 4 equiv of triphenylphosphine leads to the allylic alkylation products **4** and **5**, respectively, in yields of 24-85% (see Scheme I). To prove the stereochemistry of the newly created double bond, **4** and **5** were converted to the olefins **6** and **7**, a net homologation of the methyl groups of geranylacetone. Lithium iodide in the presence of sodium cyanide effected decarbomethoxylation in 77-78%.[7] Reductive desulfurization was achieved after protecting the carbonyl group in an overall yield of 47-67%.[8] Vpc and nmr characteristics



Scheme I
Alkylation of π-Allylpalladium Complexes



[a] NaH, $CH_3SO_2CH_2CO_2CH_3$, THF, 25°. [b] $LiI \cdot 3H_2O$, NaCN, DMF, 130°. [c] $HOCH_2CH_2OH$, PhH, TsOH, reflux. [d] Li, $C_2H_5NH_2$, 0°. [e] H_2O, HCl.

allowed the assignment of **6b** and **7a** as the major isomers. It has been shown that, in this series of compounds, cis isomers have shorter vpc retention times than trans.[6] The retention times for **6a** and **6b** are 14.4 and 13.6 min, respectively. Compounds **6b** shows a greater europium(+3) induced shift of the methylene group at C-7 than the methylene protons of the ethyl group. This observation implies a closer proximal relationship of the former methylene group to the carbonyl group. Finally, **7a** shows a single absorption in the nmr spectrum for both olefinic methyl groups, whereas **7b** is known to show two peaks for these groups.[9] As indicated before, the chemical shifts of methyl groups on trisubstituted double bonds has been shown to be diagnostic of olefin geometry.[6]

This study demonstrates the high regiospecificity of both the complex formation and alkylation. Furthermore, the stereochemistry of the newly formed double bond mainly reflects the stereochemistry of the π-allyl complex. More significantly, the method allows selective alkylation at the allylic site without the need to protect the carbonyl. The ability to create more complex structures with moderate stereospecificity and high chemospecificity from simple olefins should prove to be a useful addition to the arsenal of synthetic reactions.

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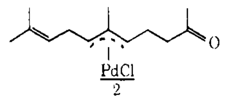
(4) In early runs without cupric chloride, an 85% yield of a mixture of **2** and **i** was obtained with only trace amounts of **1** or **3**. However, **i** has not been found in later preparations.



i

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