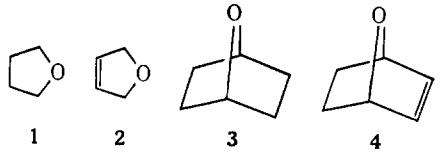
study of π_{CC},n_O interactions in unsaturated ethers. The measured ionization potentials (IP's) for the compounds studied are given in Table I.[6]

Table I. Vertical Ionization Potentials (eV)[a] of Ethers **1–4**

Tetrahydrofuran (**1**)	2,5-Dihydrofuran (**2**)	7-Oxabicyclo-[2.2.1]heptane (**3**)	7-Oxabicyclo-[2.2.1]heptene-2 (**4**)
9.57	9.14	9.57	9.44
	10.59		9.83
10.0[b]	11.4[b]	10.4[b]	10.9[b]

[a] Ionization potentials (±0.02 eV) are measured relative to the IP's of methyl iodide at 9.52 and 10.14 eV; F. Brogli and E. Heilbronner, *Helv. Chim. Acta*, **54**, 1423 (1971). [b] This band includes several ionizations. The figure quoted is the adiabatic value of the lowest IP.

The first IP of tetrahydrofuran (**1**) at 9.57 eV is readily assigned to ionization from one of the oxygen nonbonding levels. This compares favorably with the first *adiabatic* IP of ethyl ether at 9.61 eV.[7] The first two IP's of 2,5-dihydrofuran (**2**) are at 9.14 and 10.59 eV. The first band is assigned to ionization from a



1 2 3 4

level which is mainly a π_{CC} orbital, and the second band is assigned to ionization from a level which corresponds mainly to the oxygen nonbonding orbital. This ordering of levels and the π_{CC},n_O mixing (*vide infra*) is corroborated by CNDO and INDO calculations.[8] The average of the first two IP's of 1,3-dioxolane is 10.37 eV[8,9] which leads to a shift of 0.8 eV due to the inductive effect of oxygen. Introducing an additional double bond in cyclohexene to give 1,4-cyclohexadiene produces a shift of 0.2 eV.[10] If we assume that similar inductive shifts apply to dihydrofuran, we obtain[11]

$$A_\pi = 9.2 + 0.8 = 10.0 \text{ eV}$$

$$A_n = 9.6 + 0.2 = 9.8 \text{ eV}$$

The mean $(A_\pi + A_n)/2 = 9.9$ eV agrees with the observed mean of $(9.14 + 10.59)/2 = 9.87$ eV. Although this crude estimation inverts the π_{CC},n_O ordering suggested by calculations,[8] it does suggest a large π_{CC},n_O interaction ($B_{\pi,n}$) and small interactions of n_O and π_{CC} levels with lower σ levels. Calculations indicate that these latter interactions are negligible.[8] Thus we conclude that $B_{\pi,n}$ is 0.8 eV which is similar to the interactions in cyclopenten-3-one,[4a] cyclohexadiene,[13] and 1,3-dioxolane.[8,9]

The first IP of 7-oxabicyclo[2.2.1]heptane (**3**) at 9.57 eV[6] is due to ionization from one of the oxygen nonbonding levels. It is well known that alkyl substitution tends to lower IP's of analogous levels and hence, on preliminary comparison of **1** and **3**, one might expect the first IP of **3** to be lower than that of **1**. However, the changes in geometry around the oxygen atom in **1** *vs.* **3** probably result in different inductive effects and different n_O,σ interactions which offset the alkyl effect. The first two IP's of 7-oxabicyclo[2.2.1]heptene-2 (**4**) at 9.44 and 9.83 eV have been assigned to ionization from a level which is mainly π_{CC} and n_O, respectively. If we again neglect the effect of interactions involving the n_O and π_{CC} levels with the σ levels,[14] then we obtain

$$-I_1 = \epsilon_\pi = A_\pi^0 + \delta A_\pi - B_{\pi,n}$$

$$-I_2 = \epsilon_n = A_n^0 + \delta A_n + B_{\pi,n}$$

or

$$\delta A_\pi - B_{\pi,n} = 0.47 \text{ eV}[15]$$

$$\delta A_n + B_{\pi,n} = 0.26 \text{ eV}$$

Taking a value of $\delta A_\pi/\delta A_n = 4$ (*vide supra*), then $\delta A_\pi = 0.6$, $\delta A_n = 0.15$, and $B_{\pi,n} = 0.1$ eV which indicates that the interaction of the π_{CC} and n_O levels in **4** is quite small, contrary to the case of **2**. In the solvolysis of 2-halo-7-oxabicyclo[2.2.1]heptanes, there was no indication of any interaction between the oxygen "lone pair" and the developing p orbital.[16] Rate effects were ascribed entirely to oxygen inductive effects. This analysis of the PES of **4** parallels the solvolysis data.

Acknowledgment. We are grateful to the National Research Council of Canada for financial grants, to Professor C. A. McDowell for advice and encouragement, to Professor E. Heilbronner for a preprint of ref 12a and for many helpful comments, and to Professor B. Rickborn for very generous samples of **4**.

(6) We note that there is some uncertainty in assigning the vertical IP where the two or more highest vibrational peaks in a band are of approximately the same intensity. Minor variations in peak intensities from instrument to instrument can possibly affect the precise assignment of the "vertical" IP. At present we feel the best way to estimate the vertical IP from, for instance, an ionization such as the first band in **3**, which contains several peaks of similar intensity, is to estimate the maximum of the band contour

(7) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 4434 (1964).

(8) A. D. Bain, M.Sc. Thesis. University of British Columbia, Vancouver, B. C., 1972.

(9) D. A. Sweigart and D. W. Turner, *J. Amer. Chem. Soc.*, **94**, 5599 (1972).

(10) P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1677 (1970).

(11) This terminology follows that recently suggested for unsaturated hydrocarbons[12a] and other systems.[12b] The value for the unperturbed π_{CC} level is $A_\pi^0 = 9.18$ eV from the PES of cyclopentene.[10]

(12) (a) E. Heilbronner, *Isr. J. Chem.*, **10**, 143 (1972); (b) personal communication, 1972.

(13) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Horung, *Tetrahedron Lett.*, 1033 (1970).

(14) In actuality, we are neglecting *differences* in the n_O,σ interactions and π_{CC},σ interactions between **4** and **3** or norbornene.

(15) The value of A_π^0 is the IP of norbornene (8.97 eV): P. Bischof, J. A. Hasmall, E. Heilbronner, and V. Horung, *Helv. Chim. Acta*, **52**, 1745 (1969).

(16) J. C. Martin and P. D. Bartlett, *J. Amer. Chem. Soc.*, **79**, 2533 (1957); for the 2-oxabicyclo[2.2.1]heptan-6-ol systems, where oxygen participation is important, *cf.* L. A. Spurlock and R. G. Fayter, Jr., *ibid.*, **94**, 2707 (1972).

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Received August 14, 1972

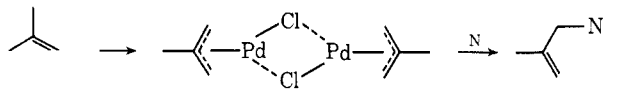
New Synthetic Reactions. Allylic Alkylation

Sir:

The activation of the α position by a carbonyl group provides the key to the most important synthetic method for formation of carbon–carbon bonds in complex molecules. The ready accessibility of many ole-

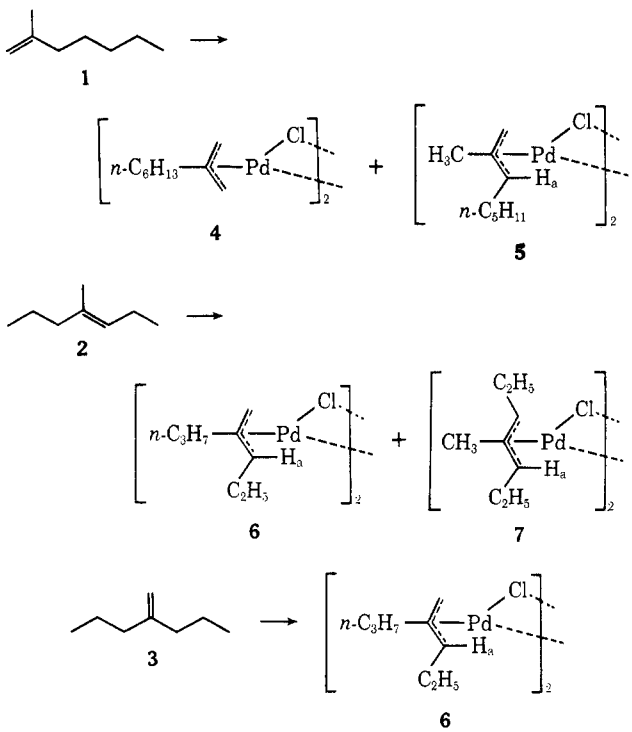
fins makes it desirable to utilize this functional group too as an activator of the α (allylic) position for alkylation reactions.[1,2] In conjunction with the problem of homologating acyclic sesquiterpenes to generate juvenile hormone derivatives, we developed a new alkylation procedure that utilizes the double bond as a direct activating group for introduction of alkyl residues.

The process involves activation of the allylic position by formation of a π-allylpalladium complex followed by condensation of this ambident electrophile with a polarizable anion as outlined in eq 1. Formation of

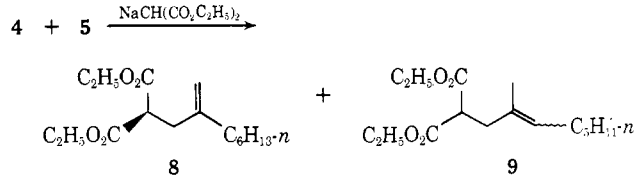


(1)

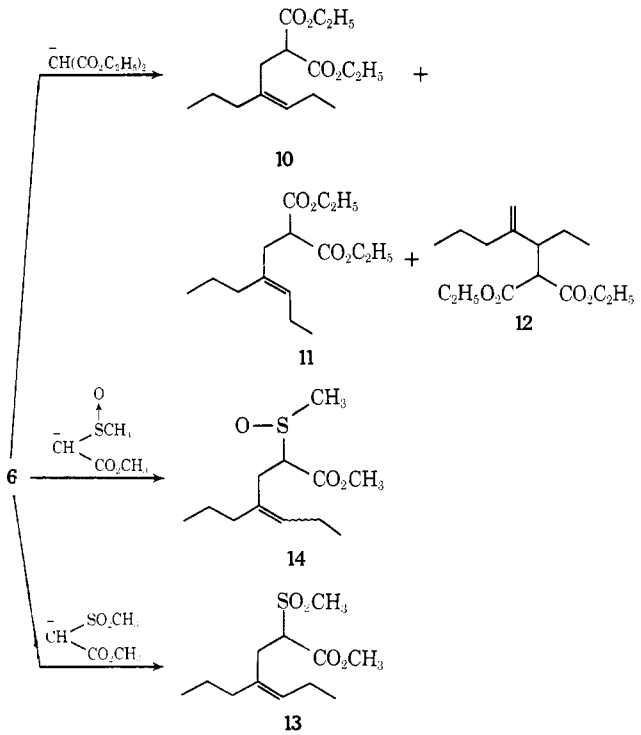
the π-allyl complex directly from the olefin can be accomplished in high yields (80–100%) by either treatment with palladium chloride in methylene chloride containing sodium carbonate (method A) or with palladium chloride and sodium chloride in acetic acid containing sodium acetate (method B).[3] In this way 2-methyl-1-octene (**1**), 4-methyl-3-heptene (**2**), and 2-*n*-propyl-1-pentene (**3**) were converted to their corresponding π-allylpalladium complexes in 100, 96, and 100% yields, respectively.[4] In the cases of olefins **1** and **2**, a mixture of positional isomers was obtained (ratio **4**:**5** 1:1.6 and ratio **6**:**7** 1:1) which could be separated by fractional crystallization. Complex **6** was the exclusive product from olefin **3**. Stereochemistry of the complexes **5**, **6**, and **7** was based upon comparison of the chemical shifts of H_a (δ 3.40, 3.52, and 3.25 for **5**, **6**, and **7**, respectively) with those reported for syn complexes.[5,6]



Initial alkylation experiments were performed with the isomeric mixture of **4** and **5**. Treatment of this mixture with malonate anion led to no reaction.[7,8] However, addition of at least 4 equiv of triphenylphosphine allowed reaction to proceed in minutes at room temperature in THF or DMF to generate the hoped-for mixture of alkylated olefins **8** and **9** in 63% yield after chromatographic purification.[4]



More detailed investigation was carried out with the homogeneous complex **6**, mp 130–131°. Treatment of the complex with the anion of diethyl malonate in the presence of triphenylphosphine led to essentially instantaneous reaction at room temperature to give a mixture of three isomers **10** (54%), **11** (34%), and **12**



(1) R. J. Crawford, W. F. Erman, and C. D. Broaddus, *J. Amer. Chem. Soc.*, **94**, 4298 (1972); C. Agami, *Bull. Soc. Chim. Fr.*, 1619 (1970); R. B. Bates, S. Brenner, W. H. Deines, D. A. McCombs, and D. E. Potter, *J. Amer. Chem. Soc.*, **92**, 6345 (1970), and references therein.

(2) For approaches to juvenile hormone by this technique, see E. E. van Tamelen and J. P. McCormick, *ibid.*, **92**, 737 (1970); R. J. Anderson, C. A. Henrick, and J. B. Siddall, *ibid.*, **92**, 735 (1970).

(3) R. Huttel and H. Christ, *Chem. Ber.*, **96**, 3101 (1963); D. Morelli, R. Ugo, F. Conti, and M. Donat, *Chem. Commun.*, 801 (1967); A. D. Kettey and J. Braatz, *ibid.*, 169 (1969); H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, **88**, 225 (1969).

(4) All new compounds were fully characterized by spectral means and satisfactory elemental compositions.

(5) K. Vrieze, C. Maclean, P. Cossee, and C. W. Hilbers, *Recl. Trav. Chim. Pays-Bas*, **85**, 1077 (1966); K. Vrieze, P. Cossee, A. P. Praat, and C. W. Hilbers, *J. Organometal. Chem.*, **11**, 353 (1968); K. Vrieze, A. P. Praat, and P. Cossee, *ibid.*, **12**, 533 (1968); J. M. Jenkins, M. S. Lupin, B. L. Shaw, and A. C. Smithies, *Proc. Int. Conf. Coord. Chem.*, **9**, 184 (1966).

(6) F. Conti, M. Donati, G. F. Pregaglia, and R. Ugo, *J. Organometal. Chem.*, **30**, 421 (1971).

(7) For a conflicting report see J. Tsuji, H. Takahashi, and M. Morikawa, *Tetrahedron Lett.*, 4387 (1965).

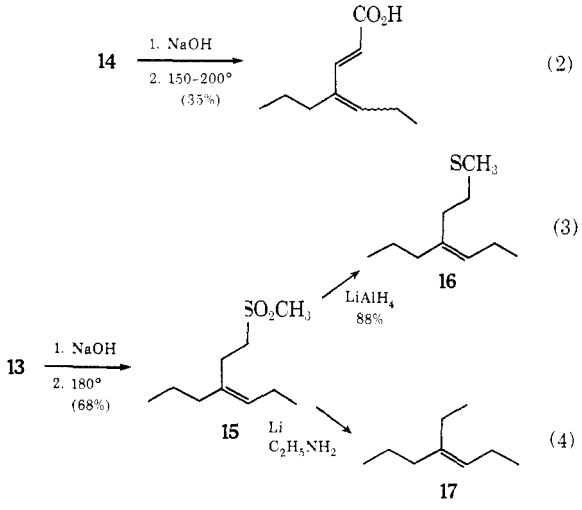
(8) See, however, W. E. Walker, R. M. Manyik, K. E. Atkins, and M. L. Farmer, *ibid.*, 3817 (1970); K. E. Atkins, W. E. Walker, and R. M. Manyik, *ibid.*, 3821 (1970); Y. Takahashi, K. Tsukiyama, S. Sakai, and Y. Ishü, *ibid.*, 1913 (1970); K. Takahashi, A. Miyake, and G. Hata, *Bull. Soc. Chem. Jap.*, **45**, 230 (1972).

(12%) in 68% yield after chromatographic purification.[4] The structural assignments are fully supported by spectral data. Thus, the alkylation introduces the new group with a preference for the less substituted end (9:1) of the π-allyl system and placement of the alkylated chain cis to the β-olefin alkyl group.

The choice of alkylating species affects both the positional selectivity and the stereochemistry. Thus, alkylation of **6** with the anion of methyl methylsulfonylacetate gave a single crystalline, mp 78°, product **13** in 80% yield.[4] The stereochemistry was assigned cis by comparison of its nmr spectrum and its $Eu(fod)_3$ shifted nmr spectrum with that of the malonate product. *In this case, the reaction proceeds completely regioselectively and stereoselectively!*

Alkylation proceeded regioselectively with the anion of methyl methylsulfinylacetate too utilizing bis(diphenyl)phosphinoethane as the palladium ligand instead of triphenylphosphine. Oxidation with sodium metaperiodate allowed correlation of this product **14** with the previously obtained **13**.[4]

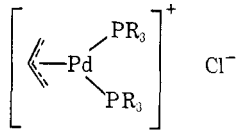
Attempts to extend the reaction to harder anions such as lithiodithiane, methyl 2-lithiomethylthioacetate, methyllithium, methylmagnesium iodide, or lithium dimethylcuprate, among others, failed. However, the sulfur stabilized anions successfully employed provide versatility for conversion to a wide range of different groups as eq 2,[9] 3,[10] and 4[11] illustrate.[4] In these



subsequent reactions, no attempt to optimize yields was made. Note that the transformation **2** → **17** represents a homologation of a methyl group into an ethyl group (a process directly applicable for the important conversion of a farnesol derivative into a juvenile hormone derivative).

Although no definitive statements regarding the course of the alkylation can be made, the requirement of 4 equiv of phosphine per dimer and the use of a soft anion led us to suggest the ionic complex **18** as an intermediate.[5] Although initial attack at carbon or palladium for this ambident electrophile cannot be differentiated at this time, we believe the requirement that the anion be a soft base favors the former.

(9) S. I. Goldberg and M. S. Sahli, *J. Org. Chem.*, **32**, 2059 (1967); D. N. Jones and M. A. Saeed, *Proc. Chem. Soc., London*, 81 (1964).
(10) F. G. Bordwell and W. H. McKellin, *J. Amer. Chem. Soc.*, **73**, 2251 (1951).
(11) W. E. Truce, D. P. Tate, and D. N. Burdge, *ibid.*, **82**, 2872 (1960); W. E. Truce and J. J. Breiter, *ibid.*, **84**, 1621, 1623 (1962).



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Acknowledgment. We wish to express our thanks to the National Science Foundation and the National Institutes of Health for their generous support of our work.

(12) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient.

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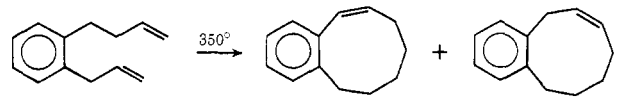
Steric Facilitation of the Ene Reaction

Sir:

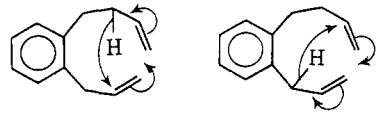
Dienes not possessing a terminal methyl group generally fail to cyclize by the ene reaction.[1] Thus 1,6-octadiene cyclizes smoothly at 457° to form a five-membered ring product, but 1,6-heptadiene is unreactive to 500°,[2] even though the ene reaction could produce a stable six-membered ring. 1,7-Octadiene[3] and 1,8-nonadiene[4] form small yields of the cyclized product, which reverts to the open-chain isomer on heating to higher temperatures. In contrast to these previous observations, we report that 4-*o*-allylphenyl-1-butene (**1**, a 1,8-nonadiene) is converted on heating at 350° for 24 hr in the gas phase to benzocyclononа-1,3-diene (**2**) and benzocyclonona-1,4-diene (**3**)[5] (eq 1),



1 2 3 (1)

in approximately equal amounts. The yield is quantitative, and the products are individually stable on exposure to the reaction conditions.

The remarkably low temperature for this reaction and the high yield of cyclized products are attributed to the constraints placed on the diene system by benzo substitution. Placement of the two ends of the diene as ortho substituents results in a very favorable steric relationship between the ene and the enophile. Both double bonds can serve in either capacity, so two benzononadienes are formed, in the manner depicted below.



To test whether steric facilitation of the ene reaction through benzo substitution is general, we prepared *o*-allylstyrene (**4**, a 1,6-heptadiene) and subjected it to

(1) For a review of the ene reaction, see H. M. R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).
(2) W. D. Huntsman, V. C. Solomon, and D. Eros, *J. Amer. Chem. Soc.*, **80**, 5455 (1958).
(3) W. R. Roth, *Chimia*, **20**, 229 (1966).
(4) A. T. Blomquist and P. R. Taussig, *J. Amer. Chem. Soc.*, **79**, 3505 (1957).
(5) Satisfactory elemental and spectral analyses were obtained on all new materials in this study. Hydrogenation of the ene products resulted in the expected known compounds.