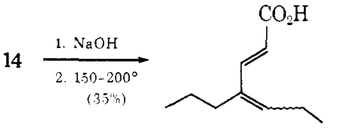
(12%) in 68% yield after chromatographic purification.[4] The structural assignments are fully supported by spectral data. Thus, the alkylation introduces the new group with a preference for the less substituted end (9:1) of the π-allyl system and placement of the alkylated chain cis to the β-olefin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

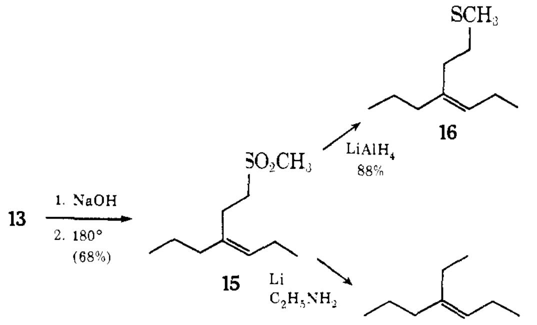
The choice of alkylating species affects both the positional selectivity and the stereochemistry. Thus, alkylation of **6** with the anion of methyl methylsulfonylacetate gave a single crystalline, mp 78°, product **13** in 80% yield.[4] The stereochemistry was assigned cis by comparison of its nmr spectrum 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).



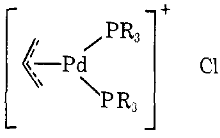
(2)



(3)

(4)

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.



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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.

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(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).

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

Barry M. Trost,*[12] Terry J. Fullerton
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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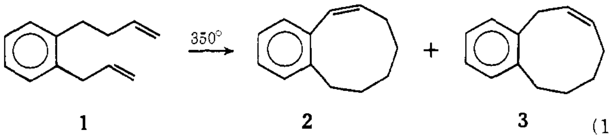
Steric Facilitation of the Ene Reaction

Sir:

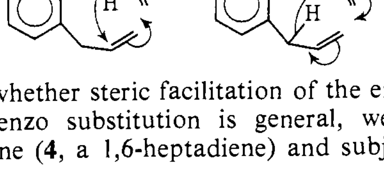
Dienes not possessing a terminal methyl group generally fail to cyclize by the ene reaction.[1] Thus 1,6-octadiene cyclizes smoothly at 457° to form a five-membered ring product, but 1,6-heptadiene is unreactive to 500°,[2] even though the ene reaction could produce a stable six-membered ring. 1,7-Octadiene[3] 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 benzocyclonona-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

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(1) For a review of the ene reaction, see H. M. R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).

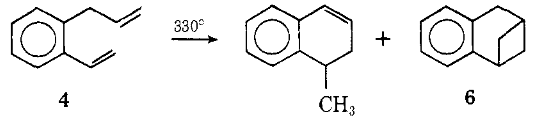
(2) W. D. Huntsman, V. C. Solomon, and D. Eros, *J. Amer. Chem. Soc.*, **80**, 5455 (1958).

(3) W. R. Roth, *Chimia*, **20**, 229 (1966).

(4) A. T. Blomquist and P. R. Taussig, *J. Amer. Chem. Soc.*, **79**, 3505 (1957).

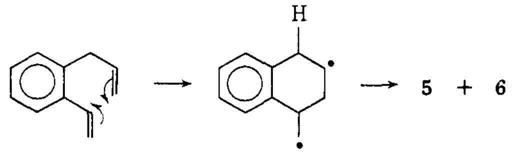
(5) Satisfactory elemental and spectral analyses were obtained on all new materials in this study. Hydrogenation of the ene products resulted in the expected known compounds.

similar reaction conditions (330°, 13 hr). Complete conversion was observed to 1-methyl-1,2-dihydronaphthalene (**5**, 90–95%) and benzonorpinene (**6**, 5–8%) (eq 2). In addition, about 1% of another ene product, benzocyclohepta-1,3-diene, was detected. All products were independently subjected to the pyrolysis conditions and found to be stable.



4 **5** **6** (2)

Only a few examples of intramolecular cycloaddition of double bonds (**6**) have been previously reported.[6] Although the dihydronaphthalene **5** can be produced through a concerted ene mechanism, the norpinene **6** requires a diradical process. The double bonds react to give the diradical **7**, which can either collapse to form **6** or undergo a hydrogen shift to complete the ene reaction that forms **5** (eq 3). A continuum of mechanisms is possible for an ene reaction, ranging from rate-determining formation of a diradical by double-bond–double-bond addition, through a concerted process, to rate-determining abstraction of the allylic hydrogen.[1] The most favorable transition state for the concerted process has the planes of the double bond (the enophile) and of the allylic system (the ene) parallel and the allylic carbon–hydrogen bond parallel to the adjacent π orbitals.[7] Because this arrangement is difficult or impossible to realize in **4**, the reaction occurs by direct closure of the closely situated double bonds to form the diradical **7**. Cyclobutane ring formation has been cited previously as evidence for a diradical ene mechanism.[3] The longer side chains offered by **1** permit the optimal arrangement for a concerted ene process. As a result, no cyclobutane product is observed.



4 **7** (3)

To summarize, we have found that intramolecular ene reactions occur very readily between ortho side chains of benzene rings, because the reactive components are constrained close to each other. The reaction mechanism, however, can vary from what is probably a concerted process when the chains are sufficiently long, to a diradical process in shorter chains when full overlap of all the necessary orbitals is not possible.

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(6) For a list of such examples, see J. Meinwald and J. A. Kapecki, *J. Amer. Chem. Soc.*, **94**, 6235 (1972); S. F. Nelson and J. P. Gillespie, *ibid.*, **94**, 6238 (1972). The structure of **6** followed from its mass spectrum (parent peak same as **4**) and nmr spectrum (no alkenic protons). Its spectra were quite different from those reported for the other possible cycloaddition product, benzobicyclo[3.2.0]heptene.

(7) See structure 122 in ref 1.

(8) This work was supported by the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 2970-AC4), and by the National Science Foundation (Grant No. GP-22942).

Joseph B. Lambert,*[8] James J. Napoli
Department of Chemistry, Northwestern University
Evanston, Illinois 60201
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Stereochemically Nonrigid Ruthenium(III) and Cobalt(III) Tris-Chelate Complexes

Sir:

We report here preliminary results of a proton magnetic resonance (pmr) investigation of stereochemically nonrigid tris(dithiocarbamato)ruthenium(III) and -cobalt(III) complexes. Tris(*N*,*N*-methylbenzyldithiocarbamato)ruthenium(III), $Ru(MeBzdtc)_3$, and tris(*N*,*N*-dibenzyldithiocarbamato)cobalt(III), $Co(BzBzdtc)_3$, have been synthesized[1] and their pmr spectra[2] recorded from −40 to +70° in CD_2Cl_2 (Figure 1) and 30 to 200° in $NO_2C_6D_5$ (Figure 2), respectively. Both complexes are stereochemically nonrigid on the pmr time scale. For $Co(BzBzdtc)_3$ the coalescence is due to intramolecular metal centered inversion ($\Lambda \rightleftarrows \Delta$), and for $Ru(MeBzdtc)_3$ the low-temperature coalescence (*ca.* −13 to +43°) also results from $\Lambda \rightleftarrows \Delta$ inversion while the high-temperature coalescence (*ca.* 43–64°) is due to S_2C–N bond rotation (*vide infra*). $Ru(MeBzdtc)_3$ is the first tris-chelate complex of ruthenium found to be nonrigid, indeed the only other ruthenium compounds reported to date which are nonrigid with respect to metal centered rearrangement are of the type H_2RuL_4[3] and $HRu(PF_3)_4^-$[4] where L is a phosphine or phosphite. $Co(BzBzdtc)_3$ is only the second tris-chelate complex of cobalt(III) found to be nonrigid with respect to inversion on the pmr time scale. The other, tris(α-R-tropolonato)cobalt(III), where R = isopropyl or isopropenyl, was recently reported.[5]

$Ru(MeBzdtc)_3$ is paramagnetic with μ_{eff} = 1.88 BM in the solid at 23°. This places the complex in the low-spin d^5 category which is the same as other $Ru(dtc)_3$ complexes (μ_{eff} = 1.74–1.88 BM).[1b] The compound is an unsymmetrical tris chelate and exists as a mixture of cis, C, and trans, T, isomers in solution. The pmr spectrum of the methyl group at −35° consists of the four expected resonances which are labeled T_1, T_2, T_3, and C (Figure 1). The C resonance is identified because the C:T ratio is slightly less than statistical. The other seven lines are due to the methylene groups. Actually eight methylene resonances are expected but two are accidentally degenerate.[6] The eight resonances derive from the diastereotopic relationship between the CH_2 protons.[6] This spectrum requires that both metal-centered $\Lambda \rightleftarrows \Delta$ inversion and S_2C–N bond rotation are slow on the pmr time scale. The total spread of the methylene resonances is 15.4 ppm. This large chemical shift difference should be compared with the spread of *ca.* 0.5 ppm observed for diamagnetic $Co(MeBzdtc)_3$[7] and results from the isotropic interaction.

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(1) These complexes were synthesized according to published procedures: $Co(BzBzdtc)_3$, (a) L. M. Compin, *Bull. Soc. Chim. Fr.*, **27**, 464 (1920); $Ru(MeBzdtc)_3$, (b) L. Malatesta, *Gazz. Chim. Ital.*, **68**, 195 (1938). This ruthenium complex is new and was purified by column chromatography using silica gel and benzene eluent. Both complexes were characterized by elemental analysis and pmr and ir spectra.

(2) All pmr spectra were recorded with a Varian XL-100-15 nmr spectrometer operated in the ^2H locked mode.

(3) P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **92**, 3482 (1970).

(4) P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muetterties, *ibid.*, **93**, 1797 (1971).

(5) (a) S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *ibid.*, **94**, 6411 (1972); (b) S. S. Eaton and R. H. Holm, *ibid.*, **93**, 4913 (1971).

(6) Two resonances result from the cis isomer which has C_3 symmetry and six (three diastereotopic pairs) from the trans which has C_1 symmetry.