Substitution at the bridgehead nitrogen also influences the stability of the 1:1 adduct. The O_2 affinities of the *N*-methyl complexes Ic and Ie are some 9–13 times greater than those of the corresponding N–H complexes Ib and Id. This is consistent with the observation that oxygen affinity is related to the electron density at the metal atom.[4,12] The increased binding constants correlate with preliminary electrochemical results.[11] The NH compounds are 80–90 mV more difficult to oxidize than the *N*-methyl compounds. By careful selection of structural parameters it is possible to obtain P_{50} values strikingly similar to those of the cobalt-substituted natural system (cf. structure Id at 2.1 °C).

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Synthesis and Absolute Configuration of Optically Active Trans-1,2-Disubstituted Cycloalkenes

Sir:

In connection with a projected synthesis of configurationally defined betweenanenes[1,2] (Scheme I) we had need of optically stable *trans*-cycloalkenes (I) of known configuration.[3] Cope and co-workers[4a] resolved *trans*-cyclooctene (I, R = H; *a* = 6) and found it to be optically stable ($t_{1/2} \sim 10^5$ years at room temperature). In contrast, *trans*-cyclononene (I, R = H; *a* = 7) rapidly racemizes ($t_{1/2} \sim 10$ s at room temperature).[4b] Alkyl substituents on the double bond would expectedly increase the rotational (jump rope) energy barrier of the *trans*-cycloalkene [(*R*)-**1** ⇄ (*S*)-**1**] thereby retarding racemization, but little is known regarding the magnitude of this effect. To establish the range of ring sizes available to us in our quest for optically active betweenanenes via routes involving cyclization (Scheme I, I → II),[5] we undertook the studies described herewith (Chart I).

We have previously shown that the bicyclic diol **1a** (X = OH), available from 2-carbomethoxycyclooctanone via Michael addition of methyl vinyl ketone followed by aldol cyclization in concentrated sulfuric acid and subsequent reduction ($LiAlH_4$), undergoes both fragmentation to dienol **2a** and reduction to alcohol **5a** upon treatment of its mono *p*-toluenesulfonate derivative I (X = $p\text{-}CH_3C_6H_4SO_3$) with lithium aluminum hydride.[6] Attempts at the optical resolution of **2a** were totally unsuccessful. However, diol **1a** (X = OH) afforded the spectacularly crystalline camphorsulfonate **1a** [white needles from ethyl acetate, mp 155–157 °C, $[\alpha]^{22}_{D} + 18.5°$ (*c* 3.23, $CHCl_3$)] in 23% yield (twice recrystallized but not optimized). Treatment of the (+)-sulfonate **1a** with lithium aluminum hydride in refluxing 1,2-dimethoxyethane for 20 h gave diene **2a** [33% yield, bp 100 °C at 0.1 Torr, $[\alpha]^{22}_{D} -35°$ (*c* 5.79, CH_2Cl_2)] and alcohol **5a** [60% yield, mp 69–70 °C, $[\alpha]^{22}_{D} -75°$ (*c* 3.61, EtOH)] with the expected spectral properties.[6]

Scheme I

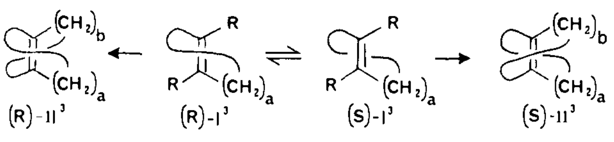
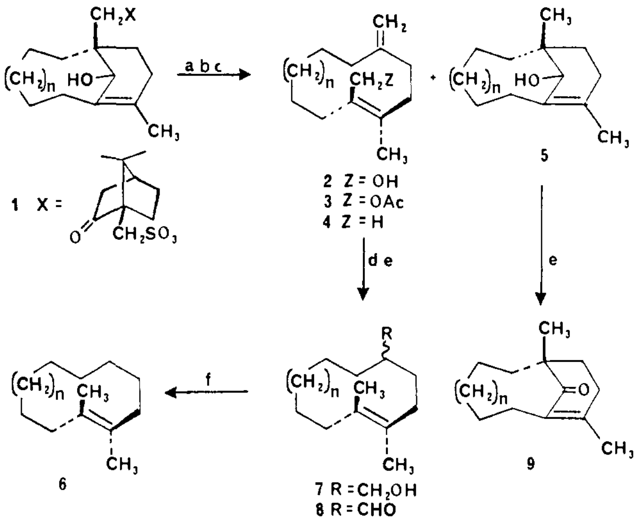


Chart I[a]



(a series, n = 1; b series, n = 2; c series, n = 3)

[a] (a) $LiAlH_4$, $MeOCH_2CH_2OMe$. (b) $(CH_3CO)_2O$, C_5H_5N. (c) Li, NH_3, THF. (d) $(Siam)_2BH$, THF; H_2O_2, NaOH. (e) $ClCrO_3H{\cdot}C_5H_5N$, CH_2Cl_2. (f) $(Ph_3P)_3RhCl$, C_6H_6.

Acetylation of alcohol **2a** and Li/NH_3 reduction of the resulting allylic acetate **3a** afforded the diene **4a** [95% yield, mp 39–40 °C, $[\alpha]^{22}_{D} -135°$ (*c* 4.71, CH_2Cl_2)]. Hydroboration–oxidation yielded alcohol **7a** (mixture of diastereoisomers) which was oxidized to aldehyde **8a** (diastereoisomers) with pyridinium chlorochromate (PCC).[7] Prolonged treatment of aldehyde **8a** with tris(triphenylphosphine)rhodium(I) chloride[8] in refluxing benzene yielded the cyclodecene **6a** [60% yield, bp 50 °C at 0.03 Torr, $[\alpha]^{22}_{D} -118°$ (*c* 2.18, CH_2Cl_2)]. The spectral properties of this material matched those of racemic *trans*-1,2-dimethylcyclodecene.[9]

The absolute configuration of olefin **6a** and its congeners was assigned through correlation with enone **9a** [bp 70 °C at 0.1 Torr, $[\alpha]^{22}_{D} +128°$ (*c* 0.72, MeOH)] secured in 94% yield via oxidation of alcohol **5a** with PCC.[7] The ORD curve of enone **9a** showed a strong positive Cotton effect at 303 nm thus establishing the *R* configuration for the quaternary center in bicyclic alkenes **9a**, **5a**, and **1a**.[10] Accordingly, the world's first optically stable *trans*-cyclodecenes[11] **2a–4a** and **6a–8a** have the *S* configuration.[3]

The bicyclic alcohol (−)-**5a** showed a sharp methyl singlet in its NMR spectrum. This signal shifted to higher field but remained intact upon addition of $Pr(facam)_3$ shift reagent.[12] Racemic **5a**, on the other hand, gave rise to two clearly distinct methyl singlets in the presence of the shift reagent. Likewise, the distinctive AB pattern of the $-CH_2OH$ grouping in alcohol (−)-**2a**[6] was shifted downfield by $Eu(facam)_3$,[12] but no new signals were produced. These experiments indicate that the

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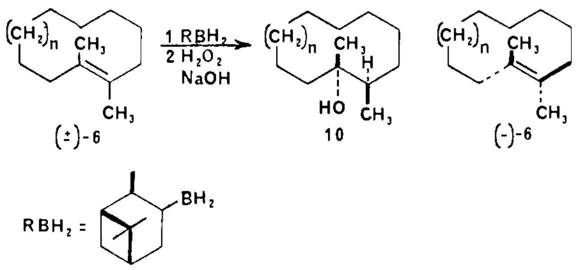
(+)-camphorsulfonate **1a** and products derived therefrom possess a high degree (>90%) of enantiomeric purity.

Following the above described sequence, the camphorsulfonate **1b** was prepared.[6] Fractional crystallization from ethyl acetate afforded material of mp 157-159 °C, $[\alpha]^{25}_{D}$ +6.4° (*c* 3.25, $CHCl_3$). Reduction-fragmentation with lithium aluminum hydride gave the diene **2b** [mp 59-61 °C, $[\alpha]^{22}_{D}$ −52.6° (*c* 6.45, EtOH)] and alcohol **5b.** Acetylation of **2b** and Li/NH_3 reduction yielded the diene **4b,** $[\alpha]^{22}_{D}$ −90° (*c* 3.28, $CHCl_3$). Selective hydroboration-oxidation followed by decarbonylation, as before, yielded (+)-*trans*-1,2-dimethylcycloundecene [**6b,** bp 190-205 °C at 750 Torr, $[\alpha]^{22}_{D}$ +29.1° (*c* 1.46, $CHCl_3$)].[13]

Enone **9b** [bp 80-85 °C at 0.2 Torr, $[\alpha]^{25}_{D}$ +109° (*c* 4.7, CH_3OH)], obtained through PCC oxidation of alcohol **5b,**[7] showed a similar ORD curve to that of **9a** indicating that it too possesses the *R* configuration. Thus olefins **2b-4b** and **6b-8b** must have the *S* configuration as shown.[3]

Efforts to prepare the bicyclo[7.3.1]tridecanediol **1c** (X = OH) met with unexpected problems, so we employed asymmetric hydroboration to assess the optical stability of *trans*-1,2-dimethylcyclododecene. Accordingly, treatment of racemic *trans*-1,2-dimethylcyclododecene (**6c**) with 0.5 mol equiv of monoisopinocampheylborane,[14] followed by oxidation with alkaline H_2O_2, afforded a mixture of alcohol **10c** [25% yield, mp 68-73 °C, $[\alpha]^{22}_{D}$ +14.9° (*c* 14.5, CH_2Cl_2)] and recovered racemic dimethylcyclododecene, $[\alpha]^{22}_{D}$ 0°. In contrast, racemic *trans*-1,2-dimethylcyclodecene (**6a**)' afforded enriched (−)-*trans*-1,2-dimethylcyclododecene [33% yield, $[\alpha]^{22}_{D}$ −18° (*c* 1.3, CH_2Cl_2)] upon similar treatment. We therefore conclude that *trans*-1,2-dimethylcyclododecene must racemize at or below room temperature.



These results show that methyl substituents on the double bond permit optically stable *trans*-cycloundecenes to be prepared.[13] Presumably bulkier substituents such as *tert*-butyl would further increase the optical stability of *trans*-cycloalkenes and thus enable isolation of even larger ring optically active homologs.

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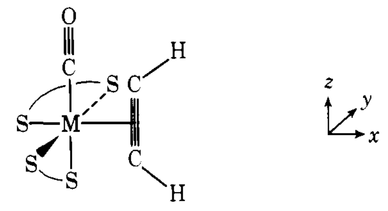
Carbon-13 Chemical Shifts of Alkyne Ligands as Variable Electron Donors in Monomeric Molybdenum and Tungsten Complexes

Sir:

The role of η^2-alkyne ligands in mononuclear metal complexes is commonly considered to parallel the Dewar-Chatt-Duncanson bonding model.[1] Properties of (η^2-alkyne)tungsten(II) complexes have recently been interpreted as manifesting electron donation not only from the acetylene $\pi_\parallel$ orbital but also from the filled acetylene $\pi_\perp$ orbital to tungsten.[2] We wish to communicate an empirical correlation between the number of electrons formally donated per alkyne ligand (*N*) compatible with an inert gas configuration for the metal center and the chemical shift of the bound alkyne carbon nuclei for a series of ten monomeric alkyne complexes of molybdenum and tungsten. The *N* values listed in Table I can be rationalized by molecular orbital considerations in each case.

The observed relationship between δ and *N* can be illustrated



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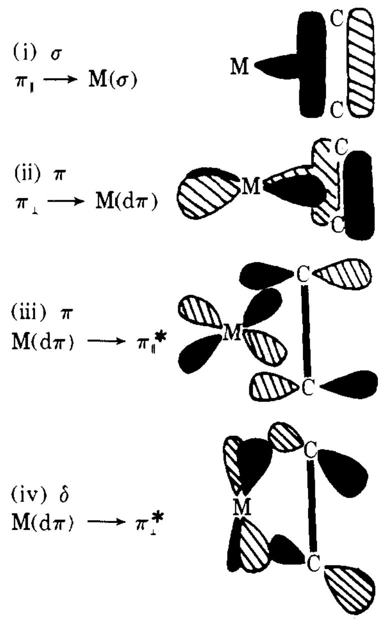

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