L' have nearly the same basicity and are small. Species I and II may be either transition states or intermediates and are not necessarily identical.

The overall mechanism is associative in nature as suggested by the following evidence. The isomerization rate decreases as L and L' increase in size and upon changing X⁻ from Cl⁻ to N₃⁻.[10] cis-[CH₃P(C₆H₅)₂]₂-PtCl₂ is converted instantaneously at 25° in CDCl₃ to trans-[CH₃P(C₆H₅)₂]₂PtCl₂ by (CH₃O)₃P, and [(CH₃O)₃-P][CH₃P(C₆H₅)₂]PtCl₂ is present in solution, whereas with (C₆H₅)₃P isomerization has not occurred for this complex within 48 hr to any measurable extent and [(C₆H₅)₃P][CH₃P(C₆H₅)₂]PtCl₂ is not present in this solution even after 48 hr. Moreover, equilibrium thermodynamics support the steric importance and solvent dependence of the mechanism.[5,10,11] This mechanism is also consistent with data obtained[5] for [(C₆H₅)₂PCH₃]₂Pd(5-CF₃-tetrazolate)₂ for which the pathway changes from (3) to (1) by addition of (C₆H₅)₂-PCH₃.

Thus, a third pathway for cis–trans-isomerization does exist and does predominate in at least some cases. We conclude, therefore, that the general mechanism contains three separate pathways whose importance varies as a function of the metal, solvent, coordinated ligand, catalyst (which may be solvent), and anion.

(11) D. A. Redfield and J. H. Nelson, *Inorg. Chem.*, **12**, 15 (1973).

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Received June 24, 1974

Chiral 1,2-Bisalkylidenecyclopentanes. Direct Formation via Cycloaddition Reactions of Chiral Substituted Alkenylidenecyclopropanes[1]

Sir:

2-Phenylisobutenylidenecyclopropane (**1**) undergoes cycloaddition reactions with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) and chlorosulfonylisocyanate (CSI) to form 1,2-bisalkylidenecyclopentane derivatives.[2,3] In a study of the stereochemical aspects of these cycloaddition reactions, (−)-(R)-**1** has been prepared[4] and reacted with PTAD and CSI at 0° in methylene chloride yielding adducts **2** and **3** and **4** and **5** respectively, *all of which are optically active.*

The configuration of **4b**, formed by the hydrolysis of **4a**, has been directly related to (+)-(S)-phenylglycine by ozonolysis and metaperiodate oxidation.[5] The absolute configuration of **2** is assigned the same as in **4**,

(1) (a) Cycloaddition Reactions of Cyclopropane-Containing Systems. VII. For the previous paper in this series see D. J. Pasto and A. F.-T. Chen, *Tetrahedron Lett.*, 713 (1973).

(2) D. J. Pasto and A. Chen, *J. Amer. Chem. Soc.*, **93**, 2562 (1971); D. J. Pasto, A. F.-T. Chen, and G. Binsch, *ibid.*, **95**, 1553 (1973).

(3) D. J. Pasto, A. F.-T. Chen, G. Ciurdaru, and L. A. Paquette, *J. Org. Chem.*, **38**, 1015 (1973).

(4) D. J. Pasto and J. K. Borchardt, *Tetrahedron Lett.*, 2517 (1973).

(5) The details of the stereochemical transformations and correlations will be reported in a future full article describing the mechanistic implications of the stereochemical studies.

(+)-(S)-2   (+)-3

(−)-(R)-1
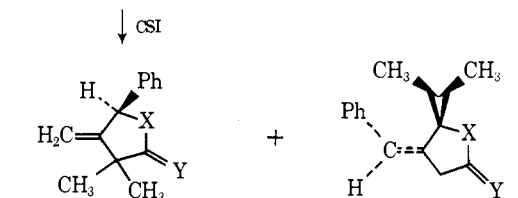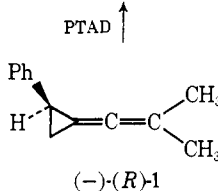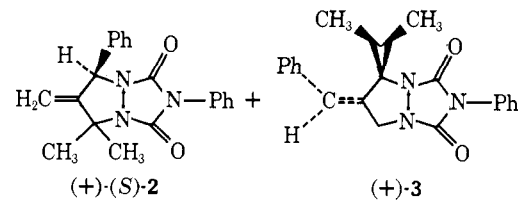
(+)-(S)-4a, X = NSO₂Cl; Y = O   (+)-5a, X = NSO₂Cl; Y = O
(+)-(S)-4b, X = NH; Y = O   (+)-5b, X = O; Y = NSO₂Cl
(+)-(S)-4c, X = O; Y = NSO₂Cl

the signs of rotation and the attachment atoms at the chiral carbon atoms in **2** and **4a** and **4b** being the same. The chirality of the dienes **3** and **5** are assigned as shown by comparison of the optical properties of the resulting PTAD adducts **6** and **7** (PTAD approaches the least

(+)-3

(−)-6

(+)-5   (−)-7
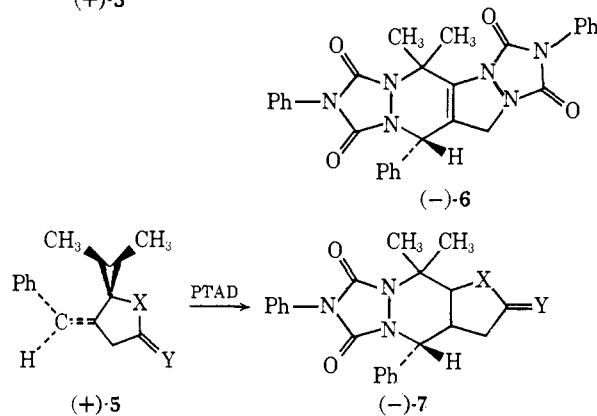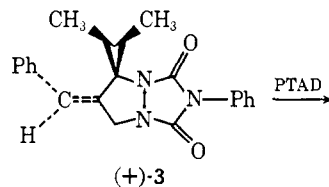
hindered face of the diene opposite the phenyl group)[2] which have opposite signs of rotation and configurations compared to **2** and **4a** and **4b**. Nmr analysis of **2** and **4b** in the presence of the chiral shift reagent tris-(trifluoroacetylcamphorato)europium(III) [Eu(tfac)₃] indicates that **2** and **4a** are formed stereospecifically.

To our knowledge **3** and **5** are the first examples of chiral, skewed 1,2-bisalkylidenecycloalkanes to be prepared. The chirality of the dienes arises from severe steric interactions between the phenyl and the "inside" methyl of the isopropylidene group forcing the diene to assume a nonplanar configuration. The extent of distortion of the diene chromophore is substantial as shown by X-ray structural studies carried out on an

adduct similar to **3**, the dihedral angle between the iso-propylidene functions being 52.3°.[6]

Passage of the phenyl past the "inside" methyl results in racemization, a process that must possess a rather high activation energy barrier.[7] Adducts **3** and **5** show no tendency to undergo racemization over the course of several. weeks at room temperature. The ease of preparation of chiral alkenylidenecyclopropanes containing a wide variety of functions attached to the cyclopropane and terminal allene carbon will allow the facile preparation of variously substituted chiral 1,2-alkylidenecyclopentanes related to **3** for structural and racemization kinetic studies. The results of such studies will complement and extend the results derived with chiral substituted biphenyls. Such studies have been initiated in our laboratories.

(6) D. J. Pasto and W. R. Scheidt, unpublished observation.
(7) Kiefer and coworkers have measured the activation energies for the racemization of a 1,2-bisisopropylidenecyclobutane and -cyclohexane deriving values of <12 and 21.1 kcal/mol, respectively: see E. F. Kiefer, T. J. Levek, and T. T. Bopp, *J. Amer. Chem. Soc.*, **94**, 4751 (1972) and references cited therein.

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Concerning the Ultraviolet Photoelectron Spectra of Osmium and Ruthenium Tetroxide

Sir:

McGlynn and coworkers[1] have recently reported He–I (21.21 eV) photoelectron (PE) spectra of the tetroxides, OsO_4 and RuO_4. The spectra were interpreted in terms of an orbital ionization sequence $3t_2 < 1t_1 < 2a_1 < 1e < 2t_2$ for OsO_4 and $3t_2 < 1t_1 < 1e < 2a_1 < 2t_2$ in the case of RuO_4. (The numbering scheme for the molecular orbitals ignores those correlating with the core orbitals of oxygen or the metal atom.) We wish to argue for an alternative assignment of the PE spectra, while pointing out that, in the case of RuO_4, the He–I spectrum contains a strong impurity band incorrectly ascribed to the ruthenium compound.

The OsO_4 spectrum reproduced by McGlynn and coworkers is in good agreement with He–I spectra measured in Oxford[2,3] (though the band system commencing at *ca.* 16 eV is poorly characterized in the published spectrum). The He–I spectra of RuO_4 are in less good agreement, however. In particular, the spectrum reported by McGlynn, *et al.*,[1] shows a band that is absent in our spectrum (Figure 1).[2b] The position of this spurious structure is indicated by the arrow in the figure.[3] The same impurity (probably CO_2) may also be responsible for a weak signal observed in the OsO_4

(1) S. Foster, S. Felps, L. C. Cusachs, and S. P. McGlynn, *J. Amer. Chem. Soc.*, **95**, 5521 (1973).
(2) (a) J. H. D. Eland, private communication, 1970; (b) S. Evans, A. Hamnett, and A. F. Orchard, unpublished work.
(3) The measurements on RuO_4 were less than straightforward since, as McGlynn and coworkers found,[1] the material has a damaging effect on channel electron multipliers. The spectra obtained on first admitting the RuO_4 vapor into the spectrometer did show the impurity band but this diminished in intensity as time progressed and eventually disappeared.
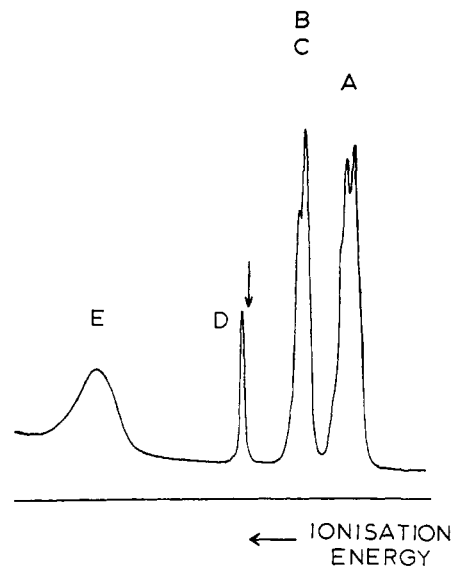

Figure 1. The He–I photoelectron spectrum of RuO_4.

spectrum at 13.87 eV ionization energy. The He–I spectra of RuO_4 and OsO_4 have also been measured by Diemann and Müller.[4] The RuO_4 spectrum was not reproduced, but the tabulated ionization energy data indicate that it is also free from the spurious band observed by McGlynn and coworkers. However, both the RuO_4 and OsO_4 spectra show an impurity band at around 15.5 eV ionization energy, which was not recognized as such by the German workers.

Our own data for RuO_4 are summarized in Table I.

Table I. Ionization Energy Data (eV) for OsO_4 and RuO_4[a]

Band system	OsO_4		RuO_4		Assignment[b]
A[c]	*12.35* 12.47 12.58 (12.68)	3.0	*12.15* 12.25 (12.35) (12.45)	3.0	$1t_1$
B	*13.12* 13.24 13.35	2.0	*12.92* (13.01) (13.10) (13.20)	2.4	$3t_2$ $1e$
C	*13.53* 13.64 13.74	1.0			
D	*14.65* 14.76	0.5	13.93	0.5	$2a_1$
E	16.40 16.76	2.0	16.1	1.7	$2t_2$

[a] The spectra, excited by He–I (21.2 eV) radiation, were measured on an instrument described by Evans, *et al.* (*Int. J. Mass Spectrom. Ion Phys.*, **7**, 261 (1971). The most intense vibrational elements are indicated by the use of *italics*. The relative band intensities (band areas) for the various band systems, normalized with respect to band A (intensity = 3.0), are given after braces. [b] The assignment is specified in terms of the molecular subshell that is ionized. [c] Band in the OsO_4 spectrum contains additional, poorly resolved vibrational structure at 12.39, 12.42, 12.45, 12.51, 12.54, and 12.60 eV ionization energy.

The correspondence between the two spectra is not entirely obvious, but we believe that the counterparts of the well-separated band systems, B and C, in the OsO_4 spectrum are unresolved in the case of RuO_4.

(4) E. Diemann and A. Müller, *Chem. Phys. Lett.*, **19**, 538 (1973).