framework. The unusual structural facet is a metal nucleus which is bonded to the carbon atom of a $-CO_2-$ group which in turn is linked through oxygen to the carbon atom in the polyhedral cage. Average bond distances are 1.97 (2) Å for Mo–C(CO), 1.16 (2) Å for C–O, 1.70 (1) Å for B–C, and 1.81 (1) Å for B–B, where the errors are based on the differences observed for chemically similar distances. The Mo–cage distances are 2.30 (1) Å for Mo–C, 2.38 (1) Å for Mo–$B_2(B_5)$, and 2.44 (1) Å for Mo–$B_3(B_4)$; shorter distances are to be expected to the more electronegative carbon atom. The Mo–CO_2–cage bonding forces the eclipsing of two carbonyls with respect to the boron atoms, but the resultant intramolecular B–C(CO) contacts of 2.89 (6) Å are not severe. The two unique $(C_4H_9)_4N^+$ ions are not disordered, but they do exhibit a considerable amount of anisotropic thermal motion.

The $-CO_2-$ linkage from C(1) to molybdenum is unique and the distances are similar to those observed in organic esters. The ester linkage is likely generated by *intra*molecular attack of an alkoxide ion formed during the reaction of class **1** ions with sodium hydride upon a coordinated carbonyl ligand. Intermolecular attack of alkyllithiums on carbonyl ligands to form coordinated "carbene" complexes is well known.[7]

The solution infrared spectra of the class **2** ions are in agreement with the X-ray structure. The terminal carbonyl bands are at lower frequencies than for the class **1** ions, consistent with the increased charge of the species, and there is a band in the ketonic carbonyl region (1660 cm^{-1} for the molybdenum complex). No hydroxyl group absorption was observed.

The class **2** ions are quantitatively converted to **1** by aqueous acid in the absence of air. This reaction involves cleavage of the ether linkage to give a simple tetracarbonyl derivative of the $B_{10}CM$ icosahedron in which there is no bonding between the carbonyl groups and the cage. All spectral data are consistent with this structural formulation. The band in the infrared spectra of the three class **1** anions attributed to OH[8] is observed in all salts and, in Nujol mulls or KBr pellets, it is sharp. In solution, the band shifts to lower frequencies and broadens. Deuteration occurs only at the OH function, and for the molybdenum complex the ratio of the OH to OD stretching frequencies is 1.2. The broad pmr resonance of the OH group appears at about τ 8 for all class **1** ions, and this resonance sharpens and shifts to lower field on addition of D_2O. The chemistry of the class **1** anions differs only in degree. The terminal carbonyl groups are relatively inert and resistant to displacement by phosphines or pyridine either under thermal or photochemical conditions. The ions are air sensitive, especially in aqueous solution, and degrade to borate. In the absence of oxygen, the class **1** ions do not react with nonoxidizing acids.

The *nido* metalloboranes of structural class **3** are formed by the action of aqueous base on either class **1** or **2** ions.[9] Addition of acid does not lead to the regeneration of class **1** or **2** ions. The $B_{10}H_{12}M(CO)_4{}^{2-}$ ions are very air sensitive, especially in acid solutions, but there is no hydrolysis in the absence of oxygen. The infrared spectrum has BH and terminal carbonyl absorptions but none attributable to hydroxyl or ketonic functions. Structurally, we believe that the class **3** ions are strictly analogous to the 11-atom icosahedral fragment metalloboranes earlier described for the $B_{10}H_{12}{}^{2-}$ complexes of metal ions derived from the group VIII and post-transition metals.[2b]

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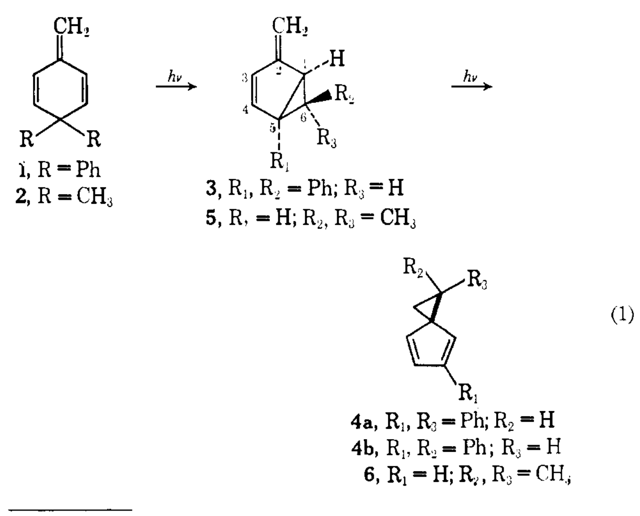
Walk Processes in Photochemical Molecular Rearrangements. A General Photochemical Transformation. Mechanistic and Exploratory Organic Photochemistry. LVII[1]

Sir:

In our description[2] of the photochemical rearrangements of 1-methylene-4,4-diphenyl-2,5-cyclohexadiene (**1**) to *trans*-5,6-diphenyl-2-methylenebicyclo[3.1.0]-3-hexene (**3**) a secondary photoproduct (**4**), shown to derive from further photolysis of product **3**, was mentioned.

We now report (1) the structure of photoproduct **4**, (2) that this product arises from a novel and general process in which a carbenoid carbon walks from one end of a butadiene moiety to the other, (3) the quantum efficiencies which are relatively independent of structure, (4) that the process proceeds only by way of the singlet-excited state, (5) the freedom of motion of the carbenoid group on the face of the π system, (6) stereochemical evidence suggesting a slither[3] mechanism, and (7) the extreme reluctance of the methylene dienone analog **2** to rearrange in contrast to acyclic di-π-methanes and cyclohexadienones.

Thus, the product of direct photolysis of *trans*-5,6-diphenyl-2-methylenebicyclo[3.1.0]-3-hexene (**3**) was shown (*vide infra*) to be 1,5-diphenylspiro[2.4]-4,6-heptadiene (**4**). Similarly, 6,6-dimethyl-2-methylenebi-



1, R = Ph
2, R = CH_3

3, R_1, R_2 = Ph; R_3 = H
5, R_1 = H; R_2, R_3 = CH_3

(1)

4a, R_1, R_3 = Ph; R_2 = H
4b, R_1, R_2 = Ph; R_3 = H
6, R_1 = H; R_2, R_3 = CH_3

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[7] E. O. Fischer and A. Maasbol, *Chem. Ber.*, **100**, 2445 (1967).

[8] A similar band was observed in spectra of the $(B_{10}H_{10}COH)_2Ni^{2-}$ ion.

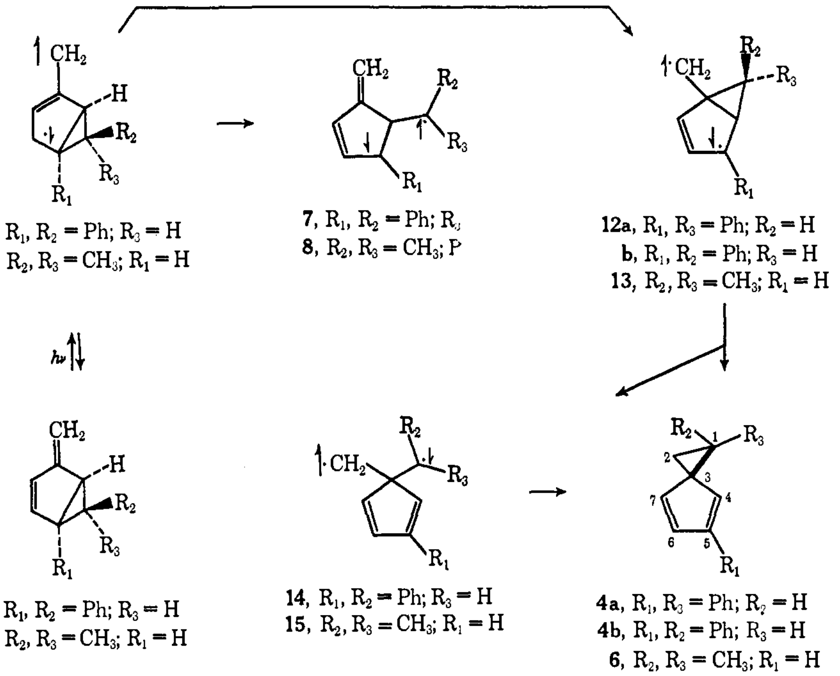
[9] Sample characterization of $[(C_3H_7)_4N]_2B_{10}H_{12}Mo(CO)_4$. *Anal.* Calcd: C, 48.2; H, 9.30; N, 4.02; B, 15.5; Mo, 13.7. Found: C, 47.9; H, 9.17; N, 4.13; B, 15.3; Mo, 13.3.

[1] For paper LVI note H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, in press.

[2] H. E. Zimmerman, P. Hackett, D. Juers, and B. Schröder, *ibid.*, 89, 5973 (1967).

[3] H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *ibid.*, 91, 434 (1969).

Chart I. Mechanism for Conversion of Bicyclic Diene to Spiro Diene



cyclo[3.1.0]-3-hexene (**5**) was found to afford 1,1-dimethylspiro[2.4]-4,6-heptadiene (**6**); *cf.* eq 1. We note that both reactants and products are formally adducts of fulvene and a carbene moiety, and the reaction involves a migration of this carbenoid carbon (*i.e.*, C-6) in eq 1 from carbons 1 and 5 to carbon 2 and the *exo*-methylene.

Reactant **5** was isolated as an intermediate in the photolysis[4] of 1-methylene-4,4-dimethyl-2,5-cyclohexadiene[4] (**2**). It was independently prepared as follows: reaction of diphenylsulfonium isopropylide and cyclopentenone gave 6,6-dimethylbicyclo[3.1.0]-2-hexanone which on selenium dioxide oxidation afforded 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one. This, with methylenetriphenylphosphorane, led to **5**.[4]

The structure of spiro-compound **4** was suggested by its nmr spectrum and confirmed by lithium–liquid ammonia cleavage to 1-phenyl-3-β-phenethylcyclopentadiene which was independently synthesized from β-phenethylmagnesium bromide and 3-phenylcyclopentenone followed by pyrolytic dehydration.[4]

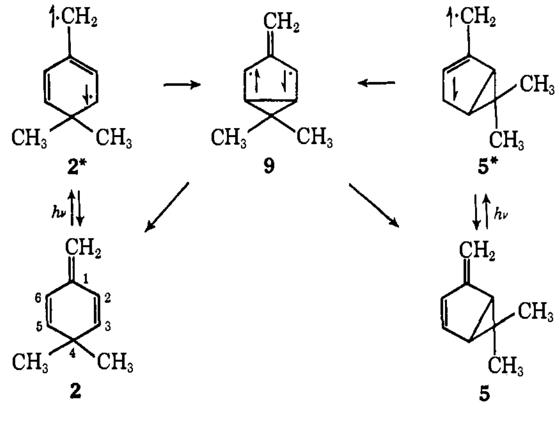
In the case of spiro-compound **6** the structure was again indicated by nmr and confirmed by synthesis from the reaction of diazocyclopentadiene with isobutylene following the general method of Moss.[5]

A first clue to the walk mechanism of the reaction leading from the bicyclic-dienes **3** and **5** to the spiro-compounds **4** and **6** derived from the very similar quantum yields for the two reactions. Quantum yields of 0.039 for the **3** → **4** reaction and 0.040 for the **5** → **6** conversion were obtained. Thus, despite the fact that one may depict the separate processes involved in the walk mechanism as shown in Chart I, it seems unlikely that the homolytic fission of bond 5,6 in the bicyclic dienes **3** and **5**, affording discrete biradical intermediates **7** and **8**, respectively, can be involved in the rate- (and quantum yield) controlling step. Were such a biradical formation to be controlling, stabilization of odd-electron centers by two phenyl groups in **7** should enhance the efficiency relative to **8**. In contrast, a mechanism in which carbon-6 of the bicyclic diene migrates concertedly along the face of the molecule should be less affected by substitution.

Furthermore, with direct quantum yields known, it was possible to proceed to the matter of multiplicity. Benzophenone sensitization established that the quantum yield of formation of **6** from the triplet of **5** was <0.0001, and that the triplet of **3** led to stereoisomerization instead of to **4**. The structure of the *cis* isomer of **3** derived from nmr analysis. This establishes that the triplet is not involved in the walk rearrangement of **3** → **4** and **5** → **6**.

Evidence was obtained that the walking carbon (*i.e.*, 6 in **3** and **5**) not only migrates from carbons 1 and 5 to the exocyclic double bond, but also from these carbons to carbons 4 and 5. Thus direct irradiation of 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene (**5**) affords 1-methylene-4,4-dimethyl-2,5-cyclohexadiene (**2**) as efficiently (*i.e.*, $\Phi = 0.038$) as it affords the spiro-product **6**. This process may be envisaged as a single walk migration to afford diradical species **9** followed by cleavage of the internal three-ring bond (note Chart II). Hence

Chart II. Mechanism for Interconversion of 1-Methylene-4,4-dimethyl-2,5-cyclohexadiene and 2-Methylene-6,6-dimethylbicyclo[-3.1.0]-3-hexene



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(4) Complete synthetic and experimental details will be given in our full paper. All compounds analyzed satisfactorily.

(5) R. A. Moss, *J. Org. Chem.*, 31, 3296 (1966).

the carbenoid carbon is seen to possess the remarkable facility to move in either direction on the surface of the π system.

Further evidence on the nature of the walk process derived from the reaction stereochemistry. Irradiation of bicyclic diene **3** was found to afford two stereoisomers, **4a** and **4b**. Proton assignments were made on the basis of spin decoupling and analysis of spin coupling. Most interesting was the chemical shifts of protons at C-4 and C-7. The synthesis and study of model compounds spiro[2.4]-4,6-heptadiene (**10**) with H-4 and H-7 at τ 4.05 and 1-phenylspiro[2.4]-4,6-heptadiene[5] (**11**) with H-4 at τ 4.26 and H-7 at τ 3.96 revealed shielding of the *syn* protons and deshielding of the *anti* protons of the C-1 phenyl group in this system. Thus, in the case of **4a** and **4b**, the isomer with the high-field H-4 was assigned *syn* stereochemistry of **4a** and the compound with the low-field H-4 was given the *anti* configuration of **4b**.

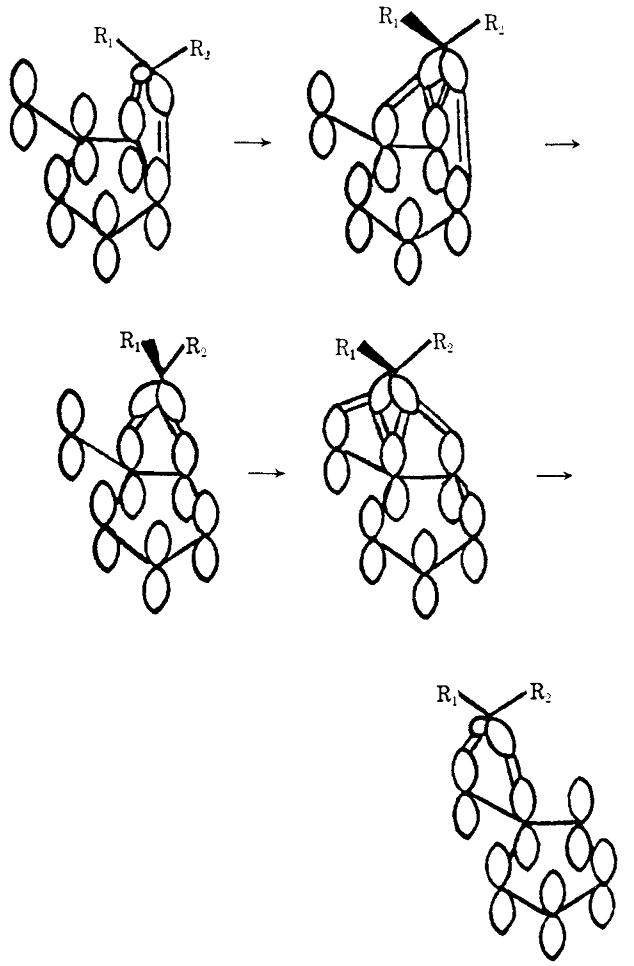
Photolysis runs beginning with the *trans*-diphenyl bicyclic diene **3** were found to give a predominance (73:27, *syn*:*anti*) of the *syn*-spiro product **4a**. However, this was due to secondary photolysis[6] as seen from runs made at lower conversions where the *anti*-stereoisomer **4b** began to predominate (30:70, *syn*:*anti*). Very facile spiroheptadiene stereoisomerization made extrapolation to zero time difficult.

This stereochemical preference in which the *endo*-phenyl group in **3** becomes *anti* in the spiro-product **4** suggests that the walk rearrangement occurs by a slither[3] process in which the diradical species in Chart I are convenient for inspecting points along the reaction coordinate but do not represent actual intermediates of finite lifetime. For example, the biradical species **7** and **8** as well as **12** and **13** are species we have previously suggested as being involved in the di-π-methane rearrangement.[1,7] However, even there the evidence was against these being discrete species.[1] Very recently an example of the conversion of a 2-methylenebicyclo-[3.1.0]-3-hexene[8] to a spiro diene has been reported and species similar to those depicted in Chart I have been considered.

A reasonable view is that the rearrangement involves a divalent carbon "slithering" along the π system in the direction of the exocyclic methylene (note Scheme I) or in the reverse direction.

Finally, we note that conversion of **2** to **5** provides the first real test of the reactivity of a methylene analog of a 4,4-disubstituted cyclohexadienone. Previously, we found[9] that 1-methylene-4,4-diphenylcyclohexadiene rearranged very inefficiently ($\Phi = 0.10$) compared with the dienone analog ($\Phi = 0.85$).[10] However, in the analog **1**, phenyl migration intervened in place of the usual dienone-like type A rearrangement. In the present case of 1-methylene-4,4-dimethyl-2,5-cyclohexadiene (**2**), no phenyl migration is possible, and a type A transformation, equivalent here to a di-π-methane rearrangement, is enforced. However, this is exceptionally inefficient ($\Phi = 0.0030$) when compared with the higher efficiency of the usual di-π-methane rearrangements (*i.e.*, $\Phi = 0.080$).[7] The efficiency difference is striking and seems to correlate with the low 3,5-bond order in the excited state of **2** relative to the acyclic systems (0.00 *vs.* 0.50 bond orders). Most remarkably, the 3,5 interaction (see Chart II for numbering) in the π–π^* excited state initially becomes slightly antibonding as this 3,5 overlap begins but then becomes more favorable with further increase in overlap. Hence, the di-π-methane rearrangement is inhibited appreciably both in theory and in fact by cyclic conjugation as in the 1-methylene-4,4-disubstituted 2,5-cyclohexadiene system.

Scheme I. Orbitals Involved in the Slither Process



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Received March 9, 1970

Rate of Water Exchange from Hydrated Magnesium Ion

Sir:

A direct measurement of the water exchange rate from Mg^{2+} at room temperature has been made possible

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(6) Note precedent for photochemical stereoisomerization of spiroheptadienes: (a) R. A. Moss and J. R. Przybyla, *J. Org. Chem.*, **33**, 3816 (1968); (b) W. von E. Doering and M. Jones, Jr., *Tetrahedron Lett.*, 791 (1963).

(7) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

(8) T. Tabata and H. Hart, *Tetrahedron Lett.*, 4929 (1969).

(9) Unpublished results of H. E. Zimmerman and P. Hackett.

(10) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967).