octahedron and the latter is bonded to only one metal and lies on or near the proper fourfold axis of the octahedron. Those forming links between two M_6 groups are denoted X^{i-i}, X^{i-a}, or X^{a-a} depending on the mode.

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John D. Corbett,* Richard L. Daake
Kenneth R. Poeppelmeier, Dennis H. Guthrie

*Ames Laboratory—USDOE and Department of Chemistry*
Iowa State University, Ames, Iowa 50011

## Diastereomeric Transition States. High and Low Energy Reaction Pathways in the Cope Rearrangement

Sir:

It has long been recognized that a variety of conformations are accessible to molecules undergoing Cope and Claisen rearrangement. The traditional chair and boat forms have now been superceded by a more thorough delineation of mechanistic possibilities.[1] An understanding of the relative energy of the individual conformations, coupled with the constraints imposed by orbital symmetry, has greatly expanded the synthetic utility of these reactions.[2] Conformationally flexible 1,5-dienes exhibit a strong preference for a presumed "chair-like" form, making independent observation of the higher energy conformations a challenging experimental task.[3] The high energy form of the Cope rearrangement has only recently yielded to independent study.[4]

We wish to report preliminary results from an investigation of the thermal rearrangements of bis(methylenecycloalkanes), eq 1, a class of molecules that permit independent observation
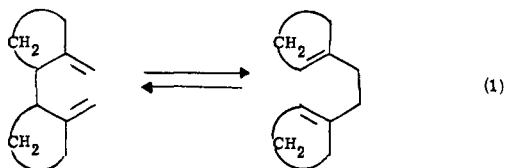
of high and low energy conformations of the Cope rearrangement. This communication describes the Cope rearrangement of *meso-* and *dl-*2-(2-methylenecyclopentane)methylenecyclopentane (**1**), eq 2. Sigmatropic rearrangement requires
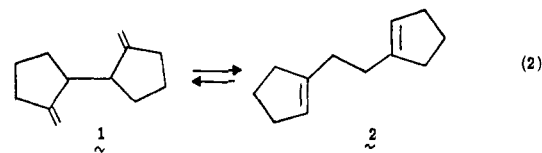
alignment of the two terminal exocyclic methylene carbons. The conformation that each diastereomer must adopt is shown in the figures in Chart I. Drawing upon the analogy of the Cope rearrangement to the dimerization of two allyl radicals,[5] the *meso-***1** transition state corresponds to the six-center approach while *dl-***1** corresponds to the four-center approach. These two transition states coincide with the high energy and low energy forms of the Cope rearrangement. This simple analysis predicts a substantial difference in the rate of Cope rearrangement for the two diastereomers. We have verified this prediction experimentally. The half-life for rearrangement of *dl-***1** at 160 °C is 1 h. Rearrangement of *meso-***1** occurs at an appreciable rate only at temperatures in excess of 250 °C. At 200 °C, *dl-***1** is 18 000 times more reactive than the meso diastereomer (extrapolated).[6]

The temperature dependence of the rate constants was examined to obtain the activation parameters for both diastereomers.[7] These, together with the activation parameters of a model compound, 2-methallylmethylenecyclopentane (**3**), and the parent, 1,5-hexadiene,[8] are given in Table I. The similarity of activation parameters between *dl-***1** and monocyclic 1,5-diene **3** should be noted. The enthalpy and entropy of activation are "normal" for Cope rearrangement.[9] Comparison of the values for *dl-* and *meso-***1** reveal sizable differences in enthalpy ($\Delta\Delta H^{\ddagger}$ 13.8 kcal/mol) and entropy ($\Delta\Delta S^{\ddagger}$ 11 eu) of activation. These differences parallel those found for the high and low energy Cope rearrangement of parent 1,5-hexadiene (Table I). Discrepancies still remain
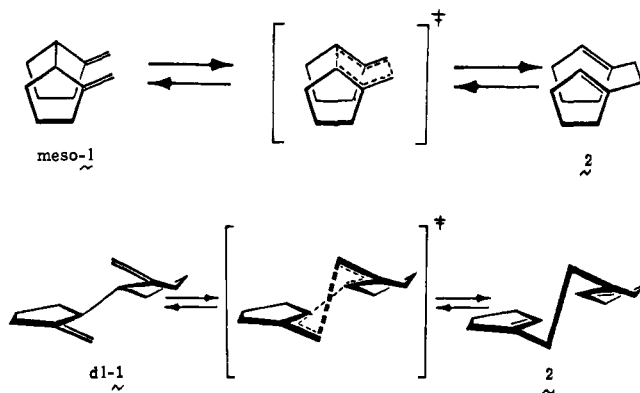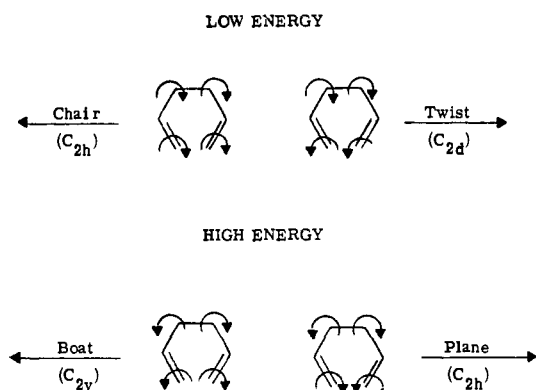
Chart I

$$\text{(2)}$$

Table I. Activation Parameters for Cope Rearrangement[a]

Compd	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}_{523}$	$\Delta G^{\ddagger}_{523}$	$\Delta\Delta H^{\ddagger}$	$\Delta\Delta S^{\ddagger}$	$\Delta\Delta G^{\ddagger}$
3	30.0 ± 0.3	−13.2 ± 1.0	36.9 ± 0.5			
dl-1	28.0 ± 1.1	−11.4 ± 2.6	33.9 ± 1.8			
				13.8	11.0	8.1
meso-1	41.8 ± 0.5	−0.4 ± 1.0	42.0 ± 0.6			
(low)[b]	33.5 ± 0.5	−13.8 ± 1.0	40.5 ± 1.0			
				11.2	10.8	5.8
(high)[c]	44.7 ± 2.0	−3.0 ± 3.6	46.3 ± 3.8			

[a] Units are in kcal/mol for $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ and cal/(mol-deg) for $\Delta S^{\ddagger}$; subscripts are in °K; uncertainties are standard deviations. [b] Reference 8. [c] Reference 4.

Chart II

LOW ENERGY

$$\xleftarrow{\text{Chair} \atop (C_{2h})} \qquad \xrightarrow{\text{Twist} \atop (C_{2d})}$$

HIGH ENERGY

$$\xleftarrow{\text{Boat} \atop (C_{2v})} \qquad \xrightarrow{\text{Plane} \atop (C_{2h})}$$

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(6) All new compounds gave satisfactory spectroscopic and elemental analysis. Their synthesis and characterization will be reported in the full account of this work.
(7) Isomerizations obeyed strict first-order kinetics. Rate constants were obtained in the liquid phase (hydrocarbon solvent) over the following temperature ranges: **3**, 160–207 °C; *dl*-**1**, 142–169 °C; *meso*-**1**, 249–285 °C.
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Kenneth J. Shea,* Richard B. Phillips
*Department of Chemistry, University of California
Irvine, California 92717*
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between the calculated[10] and experimental values of this energy difference.

Rearrangement of *meso*-**1** can be envisioned as occurring by one of several mechanistic pathways. Two such possibilities, dissociation–recombination and sequential 1,3-sigmatropic rearrangement, can be ruled out. Thermolysis of *meso*-**1** in liquid cumene failed to produce detectable quantities of either 1-methylcyclopentene or methylenecyclopentane. Furthermore, when the thermolyses were run in the gas phase, **4** could

4
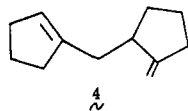
not be detected, despite the fact that **4** was shown to be stable to the reaction conditions. These findings imply that both *dl*- and *meso*-**1** react by a [3.3] sigmatropic shift; [1.3] sigmatropic rearrangement and homolytic dissociation are higher energy processes.

It is now recognized that there are two symmetry allowed variants of both the low and high energy [3.3] sigmatropic rearrangement.[1] The low energy form involves a conrotatory twisting of adjacent methylenes while, in the high energy form, rotation is disrotatory. The two variants of each form refer to the manner in which the conrotatory or disrotatory modes are coupled. The four possibilities are shown in the figures in Chart II (mirror images excluded). An intriguing aspect of the Cope rearrangement of diene **1** is the recognition that the most accessible conformations for rearrangement are not the chair and boat forms, but rather the less conventional twist (*dl*-**1**) and plane (*meso*-**1**) forms. In view of the similarity of the activa-

Twist (*dl*-**1**)   Plane (*meso*-**1**)
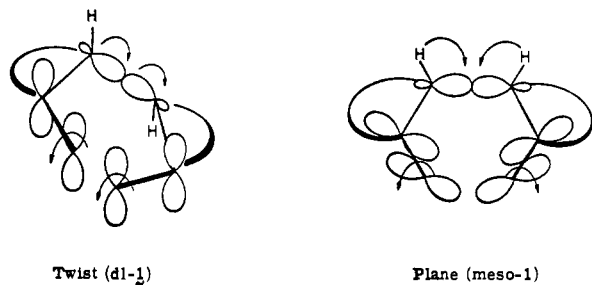
tion parameters of **1** and parent 1,5-hexadiene, the twist and plane mechanisms must be considered viable alternatives to the chair and boat forms in thermal rearrangements of conformationally flexible 1,5-hexadienes.

References and Notes

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Photochemistry of Alkyl Halides. 6. *gem*-Diiodides. A Convenient Method for the Cyclopropanation of Olefins[1]

Sir:

Recent studies from these laboratories have shown that alkyl bromides and iodides afford ionic, as well as radical, intermediates on irradiation—via a process thought to involve initial light-induced homolytic cleavage of the carbon–halogen bond, followed by electron transfer within the resulting radical pair cage (eq 1).[2] We wish now to report that *gem*-diiodides exhibit analogous behavior; however, under appropriate conditions carbenoid behavior prevails instead.

$$R\text{-}X \xrightarrow{h\nu} [R\cdot X\cdot] \xrightarrow[\text{transfer}]{\text{electron}} [R^+ X^-] \qquad (1)$$
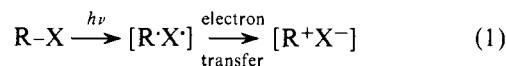
As summarized in Table I, irradiation of diiodide **1** in a variety of solvents at 350 nm afforded principally the ionic product **4**, accompanied by small amounts of the radical product **2**. In acetonitrile containing lithium bromide or in methanol the nucleophilic substitution product **3** (Y = Br) or **5** was formed in substantial amounts at the expense of elimination product **4**. This behavior is analogous to that observed previously for monoiodides.[2]

Table I. Irradiation of Diiodide **1**[a]

Solvent	Time, h	Yield, %[b]			
		1	**2**	**4**	Other
$(C_2H_5)_2O$	12	28	6	51	
C_6H_6	20	20	c	62	
CH_3CN[d]	10	40	c	10	**3**, 15[e]
CH_3OH	5	32	3	8	**5**, 45
CH_2Cl_2	1.5	10	c	39	**7**, 28
CH_2Cl_2[f]	1.0	c	5	83	**6**, 10
CH_2Cl_2[f,g]	1.5	5	4	70	**6**, 9
$(CH_2Cl)_2$	1.5	4	c	40	**7**, 33
CH_2Br_2	1.5	4	c	46	**7**, 41

[a] Irradiations were conducted on 5-mL solutions containing 50 mg of diiodide **1** in Pyrex vessels suspended in a Rayonet RPR-100 photochemical reactor equipped with a circular array of 16 G8T5 BL lamps. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. [c] Trace. [d] Solution contained 4.5 mol equiv of lithium bromide. [e] Cyclohexanecarboxaldehyde was also obtained (14% yield). [f] Solution contained 2 mol equiv of epichlorohydrin. [g] Diiodide **1**-*d* was used.