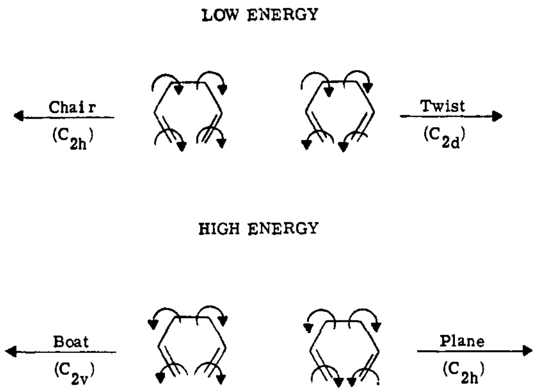
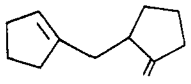
Chart II



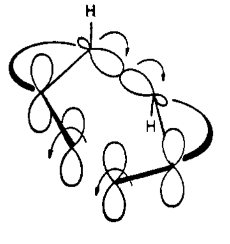
between the calculated[10] and experimental values of this energy difference.

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 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.

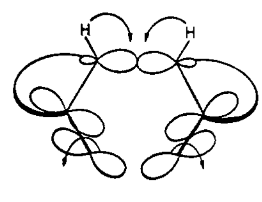


4

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 activation 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.



Twist (dl-1)



Plane (meso-1)

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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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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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.

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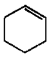
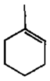
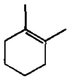
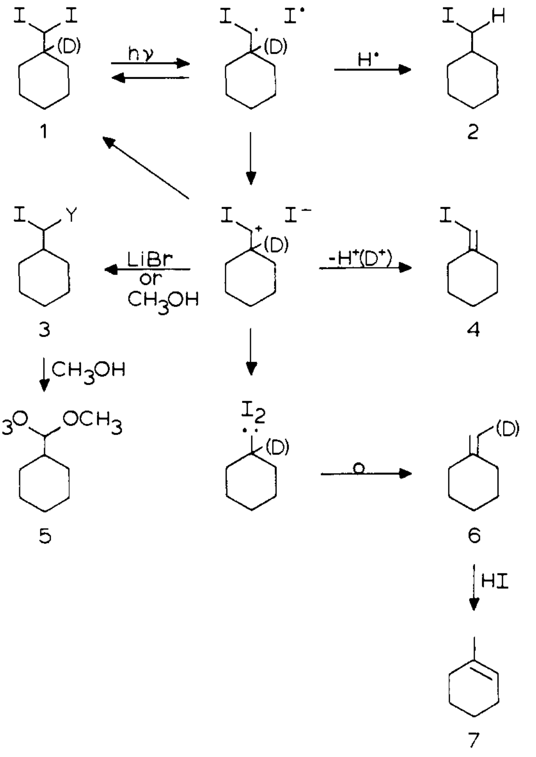
Table II. Relative Reactivities

Method				
CH_2I_2, $h\nu$	0.3	1.0	3.6	8.7
CH_2I_2, Zn(Cu)	0.14[a]	1.0	2.14[b]	0.58,[a] 0.94[b]

[a] E. P. Blanchard and H. E. Simmons, *J. Am. Chem. Soc.*, **86**, 1337 (1964). [b] B. Rickborn and J. H.-H Chan, *J. Org. Chem.*, 32, 3576 (1967).

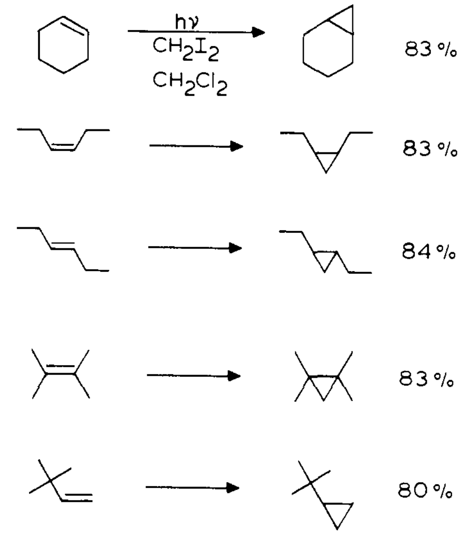
Scheme I



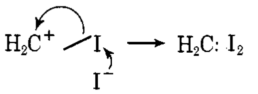
Of particular interest, however, is the fact that in a number of solvents appreciable quantities of the hydrocarbon product **7** were formed. Careful monitoring revealed that the initial product was in fact methylenecyclohexane (**6**), which was rapidly isomerized under the reaction conditions to the thermodynamically more stable **7**. When the irradiation was conducted in the presence of epichlorohydrin as an acid quencher only isomer **6** was observed. A likely origin of **6** is rearrangement of a carbenoid precursor, as shown in Scheme I. This was substantiated by the observation that diiodide **1**-*d* (95% d_1) afforded **6** with retention of deuterium (89% d_1), which was shown by ^1H NMR analysis to be located at least principally at the vinyl position.[3] The clear involvement of carbenoid photobehavior in a *gem*-diiodide is contrary to previous conclusions.[4]

gem-Diiodides which are structurally incapable of undergoing competing elimination to a vinyl iodide should display principally carbenoid behavior. Hence the previously studied irradiation of methylene iodide in the presence of olefins[4,5] has been reinvestigated and has been found under the appropriate conditions to be a convenient method for the cyclopropanation of olefins, one which complements the familiar Simmons-Smith procedure. As summarized in Chart I, irradiation of methylene iodide in the presence of a variety of olefins afforded the corresponding cyclopropane adducts in high chemical yield.[6] In a methylene chloride solution which was 0.07 M in methylene iodide and in cyclohexene, the quantum yield for disappearance of methylene iodide was 0.36 and for appearance of norcarane was 0.14. *cis*- and *trans*-3-hexene underwent cyclopropanation with complete retention of stereochemistry.

Chart I



The relative reactivities observed for a series of olefins are given in Table II. Reaction was facilitated by increasing alkyl substitution. Moreover, in contrast to the Simmons-Smith procedure, in which the steric bulk of the zinc reagent results in a diminished reactivity toward tetrasubstituted olefins and such hindered olefins as *tert*-butylethylene, the present process displayed little sensitivity to steric effects. This would be consistent with methylene as an intermediate, but the high degree of selectivity shown in Table II and the absence of C-H insertion products suggest that the intermediate is not a free carbene.[7] We tentatively propose involvement of the iodine complex resulting from nucleophilic attack by iodide ion as shown in eq 2.[8] Because of its insensitivity to steric effects, the



$$H_2C^+ \diagup I \quad I^- \longrightarrow H_2C{:}I_2 \qquad (2)$$

photochemical method complements the Simmons-Smith procedure and has a number of useful synthetic applications. Work continues on elucidating the mechanism of reaction and on extending the cyclopropanation procedure to other unsaturated substrates and to other *gem*-diiodides structurally incapable of undergoing competing elimination.

Acknowledgment. Generous financial support by the National Science Foundation is gratefully acknowledged.

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(2) P. J. Kropp, G. S. Poindexter, N. J. Pienta, and D. C. Hamilton, *J. Am. Chem. Soc.*, **98**, 8135 (1976).

(3) The observed effect of solvent on the presence or absence of carbenoid behavior is most likely attributable to the effect of solvent basicity on the rate of elimination to the vinyl iodide, relative to the rate of collapse of the ion pair to the carbene-iodine complex. There is a separate solvent effect on the rate of disappearance of diiodide on extended irradiation which correlates with the extinction coefficient for absorption at 350 nm by accumulated iodine in various solvents.

(4) R. C. Neuman, Jr., and R. G. Wolcott, *Tetrahedron Lett.*, 6267 (1966), were unable to detect carbenoid photobehavior in several *gem*-diiodides, probably because of their choice of conditions.

(5) D. C. Blomstrom, K. Herbig, and H. E. Simmons, *J. Org. Chem.*, **30**, 959 (1965).

(6) Irradiations were conducted on 10-mL methylene chloride or 1,2-dichloroethane solutions containing 0.5 mmol of olefin and 1.5 mmol of methylene iodide in a Pyrex round-bottomed flask equipped with a magnetic stirring bar, condenser, and nitrogen inlet tube, and suspended 6 cm from either a Hanovia 450-W medium pressure mercury arc equipped with a reflector or a General Electric Model RS sun lamp. The solutions were stirred with 3 mL of an aqueous solution containing 10% sodium thiosulfate and 10% sodium bicarbonate.

(7) Control studies have shown that products previously attributed to C-H in-

sertion[5] are in fact secondary products which can be eliminated by scavenging for iodine and hydrogen iodide.

(8) The alternative possibility of direct formation of the carbene-iodine complex from *gem*-diiodides is less consistent with the presence of competing elimination and nucleophilic substitution reactions and with the fact that scavengers for hydrogen iodide resulted in substantially decreased carbenoid behavior by 1.

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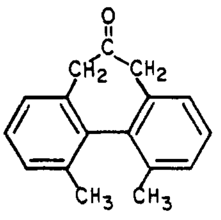
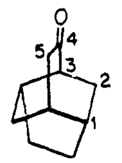
Stereoelectronic Control in the Base-Catalyzed H-D Exchange Reaction of Twistan-4-one

Sir:

Recent research activities in a number of areas have added to our understanding of the sensitivity of reaction rates to stereochemical influences. Both x-ray data[1] and theoretical calculations[2] indicate a clearly defined path of minimum energy for the attack of a nucleophile on a carbonyl group. The stringent constraints upon this reaction have led to Baldwin's approach vector analysis method of predicting the stereochemistry of the addition products.[3] In amide and ester hydrolysis, the selective cleavage of the tetrahedral intermediates has been shown by the extensive studies of Deslongchamps and co-workers[4] to be controlled by stereoelectronic[5] effects. Their work was also reinforced by theoretical calculations.[7] In contrast, one of the earliest proposals of stereoelectronic control remains a subject of controversy. The preference for axial over equatorial attack in the protonation of cyclohexenols was attributed by Corey and Sneen[8] to the necessity for proper orbital alignment in the enol fragment during protonation. Subsequent work has both reinforced[9-11] and contradicted[12-15] this interpretation. Perhaps the strongest evidence against stereoelectronic control has been the lack of selectivity in the base-catalyzed H-D exchange of conformationally biased ketones, the axial:equatorial rate ratio being between 5:1[11] and 3.5:1[15] for exchanges of 4-*tert*-butylcyclohexanone. Work in our laboratories showed much greater selectivity (75:1) in the exchange of the bridged biaryl ketone **1** as a conformationally fixed substrate,[16] although some ambiguity in the interpretation arises from the possibility of selective stabilization by the benzene rings.



1



2

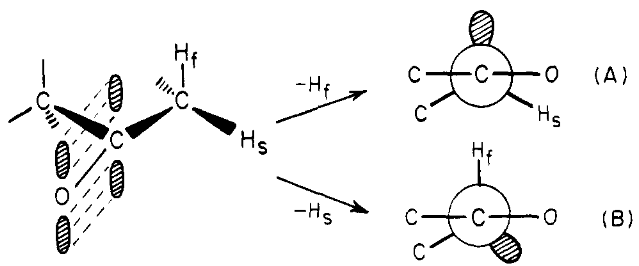


Figure 1.

In this paper, we wish to describe the observation of a kinetic selectivity of 290:1 in the base-catalyzed exchange of the diastereotopic protons α to the carbonyl group in twistan-4-one (**2**[17]). The observation of such a highly selective exchange process clearly shows that the principle of stereoelectronic control can be of major importance in the reaction of an α ketocarbanion.

The conformational properties of twistan-4-one make it an interesting subject for this stereochemical investigation. A Dreiding model of **2** shows the CH_2-CO fragment oriented so that one of the C-H bonds is aligned to permit maximum overlap with the adjacent π orbital of the carbonyl function, while the other C-H bond is held 60° out of this alignment as in the perspective formula in Figure 1. When a sample of twistanone[18] was treated with sodium methoxide (0.093 M) in methanol-*O-d*, the relative rates of exchange of the diastereotopic protons α to the carbonyl were found to be in the ratio 290:1. The rate data is given in Table I.

The assignment of the more rapidly exchanging proton to that labeled H_f (H_{fast}) in Figure 1 was made by ^{1}H NMR. A Dreiding model indicates a dihedral angle of 80° between H_f and the bridgehead proton at C-6. According to the Karplus equation,[19] a coupling constant of <1 Hz would be expected between these protons. For its diastereotopic partner (H_s), a coupling of at least 4 Hz would be anticipated. The 100-MHz spectrum of **2** (0.2 M in furan) shows a doublet at δ 2.35 (J = 15 Hz) and a quartet at δ 1.95 (J = 15 and 4 Hz) for the protons at C-5. It is the doublet at δ 2.35 with no observable vicinal coupling which first disappears on deuteration and is thus assigned to H_f as in Figure 1.

The observed selectivity of 290:1 could, in principle, be the result of (a) steric effects, (b) stereoelectronic control, or (c) preferential internal return.[20] To test for a steric effect, the rates of exchange of H_f and H_s in **2** were also determined using sodium phenoxide as catalyst. Involvement of the bulkier phenoxide base[16,21] would be expected to alter the selectivity if a steric effect were present. As the data in Table I show, there is no change in selectivity when sodium phenoxide is used as base. This indicates the absence of any significant steric effect.[22]

To test for the presence of internal return is more difficult. Although the probability of internal return occurring in methanol appears slight,[23] any discussion of the observed

Table I. Rates of Exchange of Diastereotopic Protons of **2**

Ketone	Base (solvent)	Concn, M	$k_f{}^a$ (h^{-1})	$k_s{}^a$ (h^{-1})	k_f/k_s (± estd error)
2	CH_3ONa (CH_3OD)	0.093	1.99	0.0068	293 ± 20
2	C_6H_5ONa (CH_3OD)	0.380	0.87	0.0031	280 ± 20
2-*5,5-d*$_2{}^b$	CH_3ONa (CH_3OH)	0.100	0.114	0.0018	63 ± 5

[a] All rate constants are reported as pseudo-first-order rate constants, measured at 29.0 °C. Each reported constant is the average of two determinations on quenched aliquots which were purified by sublimation prior to analysis for deuterium by mass spectral analysis. The fast reaction was followed by monitoring loss of starting material, the slow reaction by monitoring formation of d_2 species, all measurements being made by determination of P, P + 1, and P + 2 peak height ratios (average of ten spectra) after correction for natural isotopic abundances. The absence of any fragmentation pathway involving loss of deuterium or the carbon bearing the deuterium justifies the use of peak height ratios. The precision in rate constants is considered to be ±4%. [b] This dideuterio derivative, prepared by exchange of **2** in CH_3OD (1.46 M in CH_3ONa) for 4 days, showed no evidence of formation of **2**-d_3 ($\leq 2\%$ by mass spectral analysis).

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