is tempting (since it would explain by surface heterogeneity[18b] the erratic variation of the ratio between 1,3- and 1,2-methyl shifts), it should be kept in mind, however, that a nonconcerted intramolecular 1,3-hydride shift is also possible. Such a shift was demonstrated during the deamination of propylamine catalyzed by acidic solution[19-21] and led to the concept of protonated cyclopropane. Spectroscopic observation of a 1,3-hydrogen shift in the 2,4-dimethylpentyl ion was also reported by Brouwer and Van Doorn.[22] Experiments with double ^{13}C and D labeling and/or the use of deuterated catalyst are required to clarify this point.

Acknowledgment. We wish to thank Mrs. Corolleur for her help in the syntheses of the labeled hydrocarbons.

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The Stereochemistry of Cycloadditions of Ketenes to Unsymmetrical Alkenes. Evidence for Nonparallel Transition States[1]

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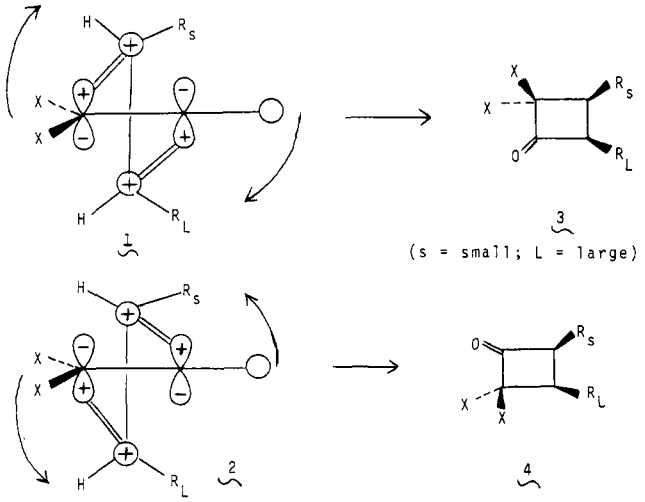
Abstract: The cycloaddition of dichloroketene to 3,3-dimethylcyclopentene (**5**), 3,3-dimethylcyclohexene, 1,5,5-trimethylcyclohexa-1,3-diene, and spiro[2.4]hepta-4,5-diene, and of diphenylketene and *tert*-butylcyanoketene to **5** has been investigated. The stereochemistry of the product cyclobutanones has been determined by chemical and spectral means, including lanthanide-induced shifts in NMR. It is shown that stereoelectronic effects guide the cycloaddition to cyclohexenes, whereas steric effects predominate in analogous cyclopentene substrates. The steric results are consistent with a nonparallel transition state for addition as required by 2s + 2a or 2s + 2s + 2s mechanisms. Cycloreversion was exhibited by the adduct of **5** with diphenylketene.

Introduction

Since the discovery[2] that dichloroketene adds readily in situ to reactive olefins to yield α,α-dichlorocyclobutanones, the reaction has been the subject of a large number of synthetic and mechanistic studies.[3] The stereospecificity of the addition,[4] as well as the regioselective addition of dichloroketene to the cyclopentene double bond of dicyclopentadiene[5] and the lack of dependence on solvent polarity[4] suggest a concerted mechanism. A $\pi 2_s + \pi 2_a$ mechanism[6] is consistent with the general results for ketene–olefin cycloadditions. In such a process, the ketene plays the antarafacial role, so that, in the case of unsymmetrically substituted ketenes, the smaller substituent is preferentially oriented toward the cyclic olefin partner and predictably becomes exo in the major product.[7]

For the interaction of a symmetrically substituted ketene like dichloroketene with a simple cyclic olefin, the geometry of the transition state cannot be deduced from the products. In the case of cyclohexenes preferential axial bonding by the ketene carbonyl has been demonstrated.[3c] Although the low reactivity of dichloroketene toward norbornene[5] has been accounted for on the assumption of hindrance to the perpendicular geometry required for a $2_s + 2_a$ process, steric effects in these cycloadditions have not been evaluated, and more conclusive proof is desirable. Hence, we felt that the reaction of a ketene with an unsymmetrically disubstituted olefin might shed light on the factors influencing the cycloaddition. The more likely transition states for such an addition are pictured in Scheme I. In the least sterically hindered approach, the ketene would be expected to approach with its carbonyl end toward the substituents as shown. The overlap depicted in **2** (leading to product **4**) should be favored over **1** (leading to **3**) because rotation of the ketene in **2** moves the carbonyl group *away* from the bulkier substituent R_L. On the other hand, if the cycloaddition proceeded by way of a (forbidden) $\pi 2_s + \pi 2_s$ process, **3** would be the expected major product on steric

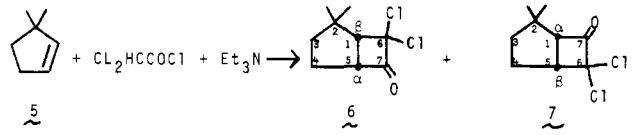
Scheme I



grounds because in a parallel transition state CX_2 would prefer to approach from the side of the smaller R_s substituent. Other factors (stereoelectronic) may also enter into consideration.

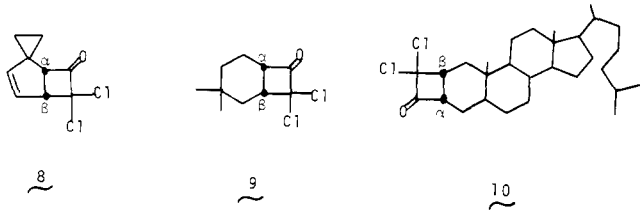
Results

1. Europium Shift Studies. We first examined the addition of dichloroketene to 3,3-dimethylcyclopentene (**5**) which can



give rise to adducts **6** and **7.** In the past it has been assumed[5] that the downfield methine resonance in dichloroketene-olefin adducts is assignable to the proton α to the carbonyl group. However, this has not been rigorously established, and, indeed, examples are described below in which this generalization does not hold. We therefore sought a method for unequivocal differentiation of adducts such as **6** and **7** without resort to lengthy chemical degradations.

In the case of dieldrin and related compounds containing epoxide and chlorine functional groups,[8] Eu(dpm)$_3$ was found to complex only with the oxygen atoms, resulting in NMR shifts which were inversely proportional to the cube of the distance of a proton from the europium atom in the complex. Although ketones complex somewhat less strongly than epoxides with Eu(dpm)$_3$,[9] one would still expect that, in the case of α,α-dichlorocyclobutanones, the shift reagent would complex with the carbonyl oxygen atoms. By utilization of the stronger Lewis acid, Eu(fod)$_3$, the shifts should be greater, and the methine proton α to the carbonyl should shift farther than the β-methine proton for a given amount of added shift reagent. To test the validity of these predictions, lanthanide NMR shifts were observed by adding Eu(fod)$_3$ to samples of three dichloroketene adducts **8, 9,** and **10** whose structures and NMR as-

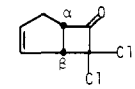


signments[10,11] had been well established. The results are presented in Table I (for further details see Experimental Section). Although the shifts are relatively small, the α-proton resonances shift farther downfield than those of the β-protons, as predicted. An adduct whose structure was known but whose

Table I. Downfield Shifts (ΔEu) in the NMR Spectra of Dichloroketene Adducts on Addition of Eu(fod)$_3$

Compd	α-H τ	α-H Δ (Hz)	β-H τ	β-H Δ (Hz)	Ratio $\Delta\alpha/\Delta\beta$
8	6.33	12	5.8	8	1.5
9	6.07	24	7.08	14	1.7
10	6.12	21	7.08	11	1.9
11	5.75	23	5.98	12	1.9
6	6.03	31	6.98	18	1.7
7	6.45	21	6.66	13	1.6
22	6.4	21	7.09	11	1.9
23	6.68	44	7.30	28	1.6
28	6.37	9	6.68	5	1.8

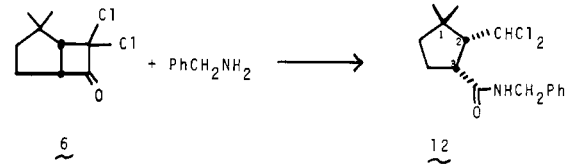
NMR assignments were not, namely **11**,[2] was then subjected



to Eu(fod)$_3$, enabling assignment of every proton in the NMR. As seen in Table I, the addition of Eu(fod)$_3$ to samples of **6** and **7** confirmed the structures assigned to these products.[12] Furthermore, the calculations of the ratio of Δ_α to Δ_β using the pseudocontact shift proportionality,[13] $\Delta\text{Eu} \propto (3\cos^2\theta - 1)r^{-3}$, and parameters from Prentice-Hall models, give values of $\Delta\alpha/\Delta\beta$ = 1.6-1.8, which correlates well with the observed ratios of 1.5-1.9 (see Table I). This method permits structural assignments to ketene-olefin adducts even in cases where only one regioisomeric product is available.

2. 3,3-Dimethylcyclopentene. Treatment of the 3,3-dimethylcyclopentene (**5**)[14] with dichloroketene at room temperature generated in 51% yield two isomeric adducts ($C_9H_{12}Cl_2O$) in a ratio of 5:1. Since cyclopentene itself is relatively unreactive toward addition of dichloroketene even when the olefin is used as the solvent,[5] dichloroketene was generated in situ in neat liquid olefin (**5**) by slow simultaneous addition of equivalent amounts of dichloroacetyl chloride and triethylamine. In this manner, the polymerization of the ketene was kept to a minimum. The major adduct exhibited, inter alia, a multiplet at τ 6.03 (1 H) and a doublet at 6.98 (J = 8 Hz, 1 H) in its NMR, while the minor adduct showed a reversal in the positions of the multiplet and doublet (τ 6.66 and 6.45). They were assigned structures **6** and **7,** respectively, on the basis of Eu(fod)$_3$ shifts.

Additional substantiation of the structure of **6** (and, hence, indirectly, of **7**) was garnered from its derivatization with benzylamine. The resulting **12** showed a doublet of doublets



in the NMR for the methine proton on C-2 adjacent to the *gem*-dimethyl substituents. Compound **7** would have given a product in which the H-2 would have appeared as a doublet.

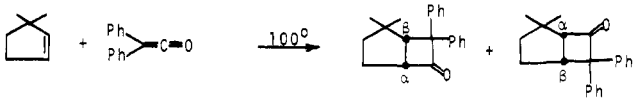
In order to ascertain that the addition of dichloroketene to olefin **5** was indeed a concerted process and was not forced into a stepwise process by the presence of the two methyl groups, we investigated the reaction of **5** with diphenylketene. The latter has been demonstrated[15] to react with olefins in a concerted manner and is much less reactive and less electrophilic than dichloroketene.[5] Hopefully, this experiment would test the perpendicular geometry of the transition state for diphenylketene, as well. In fact, treatment of **5** (in 100% excess)

Table II. Downfield Shifts[a] (ΔEu) in the NMR Spectra of Nonchlorinated Cyclobutanones

Compd	α-H		β-H	
	τ	Δ (Hz)	τ	Δ (Hz)
13	6.39	190	6.72	96
14	6.79	160	6.27	76
15	6.88	110	5.93	78
18	6.72	194		

[a] For further details, see Experimental Section.

with diphenylketene at 100 °C in a sealed tube for 11 days resulted in a 90% yield of adducts **13** and **14** in a ratio of 5.7:1.

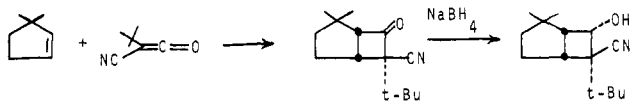


5 **13** (major) **14**

Adduct **13** was characterized by a doublet (J = 9 Hz) at τ 6.72 (H-1), upfield from the H-5 multiplet at 6.39, and, most convincingly, by strong shielding (τ 9.54) of the *endo*-CH_3 by the *endo*-Ph substituent. Surprisingly, the H-1 doublet (J = 7.5 Hz) for **14** at τ 6.79 was *also* upfield from the H-5 multiplet at 6.27. The structural assignments were confirmed, however, by means of Eu(fod)$_3$ as shown in Table II.

Adduct **13** started to dissociate into olefin **5** and diphenylketene at 135 °C, and at 200 °C in hexachlorobutadiene the retrocycloaddition was rapid, with a half-life of about 15–20 min. None of the isomer, **14**, was formed, and the latter is not affected under the same conditions. Thus, **13** is indeed a kinetic product and does not equilibrate with **14**, which is expected to have a lower free energy on steric grounds.

The cycloaddition of 3,3-dimethylcyclopentene **5** (in excess), with *tert*-butylcyanoketene[7b] at 25 °C provided in good yield a crude product which appeared to be only one stereoisomer. Although the H-1 doublet (J = 9 Hz) at 6.88 was upfield from the H-5 multiplet at 5.93, the former was shifted farther by Eu(fod)$_3$ (see Table II), and, again, as for **14**, the relative positions were *reversed* when enough shift reagent was added. The location of the *tert*-butyl and cyano functions was determined by reducing the adduct with sodium borohydride. The resulting alcohol, **16**, showed two doublets of doublets in the



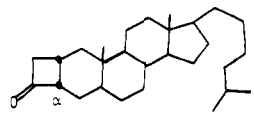
5 **15** **16**

NMR: the H-1 appeared at 6.22 with J = 9 and 11 Hz, and the H-7 gave rise to J = 4.5 and 11 Hz at 5.78. Such coupling is consistent with cis hydrogens on the cyclobutane ring[7b] and with the indicated regiochemistry. Furthermore, addition of Eu(fod)$_3$ to **16** shifted the *tert*-butyl singlet farther than the *exo*-CH_3 but not as far as the *endo*-CH_3 singlet. These data are uniquely in accord[16] with structure **15** for the ketene adduct. *The reversal of the regiochemistry for cycloaddition of this ketene* from that observed for dichloro- and diphenylketene is of great interest and is discussed below in the Discussion section. The stereoselectivity for the *endo-tert*-butyl is expected (see Introduction) for a $2_s + 2_a$ mechanism of addition and has been previously observed.[7b] The endo stereochemistry of the *tert*-butyl group was confirmed by a low-temperature NMR study of **15**. The *tert*-butyl singlet broadened considerably between ca. −40 and −71 °C, as reported[17] for compound **17**, in which the *tert*-butyl is almost exactly as

17

close to the adjacent methyl as the *tert*-butyl in **15**, is to the adjacent CH_2 of the five-membered ring.

In an ancillary experiment, the unsubstituted steroidal cyclobutanone, **18**,[11] was treated with Eu(fod)$_3$ to better gauge



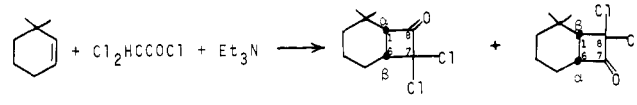
18

the effect of substitution on the shifts. Although only the H-3 (α) proton could be observed separately from the rest of the protons, its shift was very large and comparable with that for the diphenyl ketone, **13** (see Table II). Furthermore, a competition between acetone and acetonitrile for Eu(fod)$_3$ revealed that acetone got complexed to a much greater extent, as judged by relative NMR shifts. Thus, our assumption of complexation of Eu(fod)$_3$ with the oxygen atoms in both **15** and **16** is reasonable.

3. 3,3-Dimethylcyclohexene. In view of the axial rule put forth for ketene cycloadditions to cyclohexenes,[3c] it seemed desirable to compare additions to 3,3-dimethylcyclohexene (**19**) with those to 3,3-dimethylcyclopentene (**5**). Compound **19** had been previously synthesized from tosylhydrazone **20** by heating it with sodium methoxide in diglyme.[18] The primary drawback of this route is the difficulty[19] in separating ketone **21** from other alkylation products. This problem was circumvented when it was found that tosylhydrazone (**20**) could be obtained pure from reaction of tosylhydrazine with a mixture of **21** and minor products resulting from a Haller-Bauer methylation[19] of 2-methylcyclohexanone. The preparation of **19** from **20** by the method of Shapiro and Heath[20] was then straightforward.

21 **20** **19**

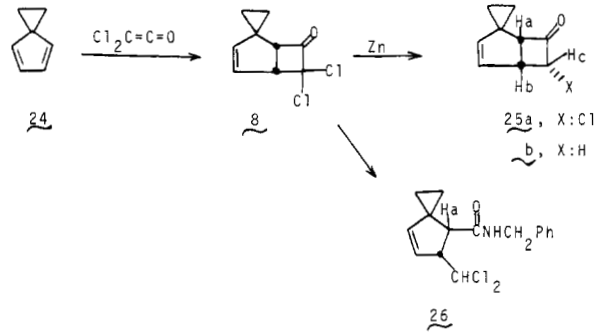
Treatment of a large excess of neat cyclohexene **19** with dichloroacetyl chloride and triethylamine under the same conditions as for cyclopentene **5** led to a 54% yield of isomeric adducts **22** and **23** in a ratio of 2.6:1. As in the case of the cyclopentene adducts **6** and **7**, the H-1 doublet (J = 10 Hz) at τ 6.4 in **22** was downfield from the H-6 multiplet at 7.09, while the H-1 doublet (J = 10 Hz) at 7.3 in **23** was upfield from the H-6 multiplet at 6.68. Addition of Eu(fod)$_3$ (see Table I) confirmed these structural assignments for the major and minor adducts, which are formed in a reverse ratio from the analogous adducts **6** and **7**. The coupling constants (half-width) for the multiplets due to the H-6 in both **22** and **23** added to ca. 30 Hz in each case, indicating an axial configuration for these protons. Hence, in adduct **22** the carbonyl-carbon bond is axial and the CCl_2–C bond is equatorial.



19 **22** (major) **23**

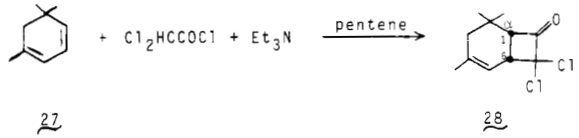
4. Dienes. It was of interest to compare the above results for the cyclic mono-enes **5** and **19** with addition of dichloroketene

to cyclic dienes in which the effect of a conjugated double bond would be added to the steric effects present in **5** and **19.** The first compound chosen for this purpose was the spiro-diene **24.**[21] Reaction of **24** with dichloroketene produced adduct **8** in nearly quantitative yield. Its structure was proved[22] by $Eu(fod)_3$-induced shifts in the NMR, as well as by ring opening to amide **26.** Zinc reduction of **8** gave mainly monochloro ketone **25a** and some ketone **25b.** The large vicinal coupling J_{ab}

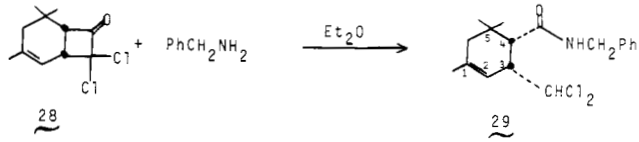


= 7 Hz and small 1,3-coupling J_{ac} = 3 Hz in **25a** are consistent with the assigned regioisomeric structure, as is the Ha doublet in amide **26.** Furthermore, Hb is shifted from τ 5.9 in **25a** into an upfield multiplet upon dechlorination to **25b.**

The second diene studied, **27,** was expected to give a higher proportion of **28,** the isomer having the carbonyl group syn to



the *gem*-dimethyl group, than was obtained from mono-ene **19.** Indeed, when diene **27**[23] was treated in pentene with dichloroketene, generated in situ by the dehydrochlorination method, a 53% yield of a single adduct, **28,** was obtained. The assigned structure was fully substantiated by NMR and $Eu(fod)_3$ shifts (Table I). In addition, treatment of **28** with benzylamine gave, along with elimination products, a small yield of the benzylamide **29.** Although a sample of **29** was not



obtained for analysis it was characterized by NMR, ir, and mass spectrometry. These results for diene **27** are summarized in Table III along with data for the other ketene additions reported above.

Discussion

The results of the addition of dichloro- and diphenylketene to 3,3-dimethylcyclopentene (**5**), as summarized in Table III, indicate that the regioisomeric cyclobutanone with the carbonyl group nonvicinal to the *gem*-dimethyl function predominates. This can be explained in terms of Scheme II with bonding (overlap) occurring preferentially as in **30** and resulting in rotation of the ketene ca. 90°, so that the carbonyl group is moved away from the methyl groups and the nonvicinal isomer is formed. The insensitivity of the cycloadduct ratios **6**/**7** and **13**/**14** to the size of the ketene substituents (chlorine vs. phenyl) is consistent with a nonparallel but not with a parallel approach of the ketene to the olefin **5.**

Scheme II

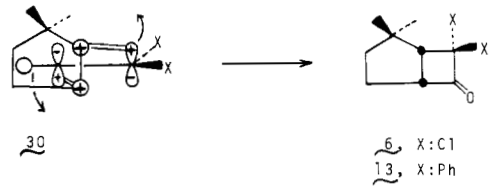


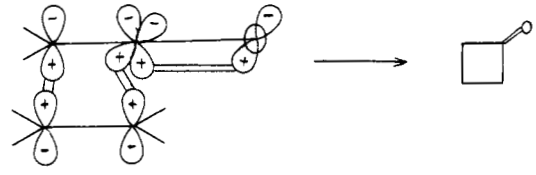
Table III. Product Ratios for Ketene–Olefin Cycloadditions

Olefin	Ketene[a]	Major adduct[b]	Minor adduct[b]	Ratio (anti:vic)
5	DCK	**6** (anti)	**7** (vic)	5.0
5	DPK	**13** (anti)	**14** (vic)	5.7
5	BCK	**15** (vic)		
19	DCK	**22** (vic)	**23** (anti)	0.39
27	DCK	**28** (vic)		
24	DCK	**8** (vic)		

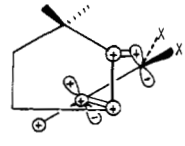
[a] DCK = dichloroketene ($Cl_2HCCOCl + Et_3N$), DPK = diphenylketene, BCK = *tert*-butylcyanoketene. [b] vic = vicinal, vic and anti refer to the relative position of the *gem*-dimethyl and carbonyl groups.

It would be satisfying to be able to state that all possibilities other than the perpendicular $2_s + 2_a$ transition state have been eliminated by these results. However, another, equally convincing, orbital symmetry allowed process has been proposed by Baldwin.[15b] This is a six electron $_\pi2_s + _\pi2_s + _\pi2_s$ cycloaddition in which one p orbital of the olefin overlaps with the terminal carbon p orbital of the ketene and the other olefin p orbital overlaps with the central p orbital of the C=O double bond. The remaining two p orbitals (the central p orbital of the ketene C=C bond and the terminal p orbital of the C=O bond) form the C=O bond of the product cyclobutanone as shown in Scheme III.[24] The most favorable geometry for this

Scheme III



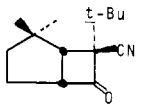
type of interaction would be a skewed one in which the ketene and olefin axes make an angle with each other and one of the ketene substituents dips toward the olefin. If the smaller substituent dips toward the olefin for steric reasons, it must become exo, just as is the case for a $2_s + 2_a$ mechanism. Furthermore, in the case of olefin **5,** as the ketene approaches the double bond, the ring carbons and the methyl groups would sterically force the ketene to assume the geometry depicted in **31.**



Bonding must then occur as shown, leading again to **6** or **13.** A choice between a $2_s + 2_a$ and a $2_s + 2_s + 2_s$ mechanism is not possible from the available data.

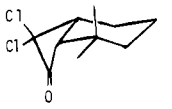
In the addition of *tert*-butylcyanoketene to **5,** as the ketene moiety rotates to form product, regardless of whether the activated complex looks like **30** or **31,** the *tert*-butyl group is forced to become endo and hence encounters severe repulsion from the *endo*-CH_3. This steric interaction prevents the for-

mation of **32** altogether and causes process **1** → **3** (Scheme I) to take place preferentially, leading to regioisomer **15.**

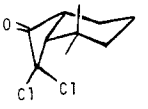


32

The reversal of regiochemical preference in the cycloaddition to cyclohexene **19** vs. cyclopentene **5** is due to stereoelectronic preferences. The addition of dichloroketene to **19** takes place preferentially in such a fashion that the bond to the carbonyl carbon becomes axial in the product, and the bond to the CCl_2 carbon becomes equatorial, **22** being the major



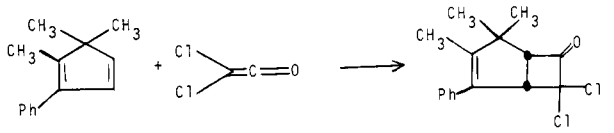
22 (major product)



23 (minor product)

product. This has been discussed[3c] in terms of stereoelectronic control and the principle of least motion leading to axial bonding by the carbonyl carbon. Apparently, for olefin **19,** this effect is somewhat but not overwhelmingly more important than the steric interaction discussed above for olefin **5.**

In the case of dienes **24** and **27** the electronic effect observed for cyclopentadiene and cyclohexadiene[5] completely overrides the steric effect of the CH_2 groups in **24** and the methyls in **27.** Thus, **24,** in opposition to monoolefin **5,** reacts with dichloroketene to give, regiospecifically, the isomer **8.** Similar behavior has been observed for diene **33,** which was recently reported[25] to give only adduct **34** in excellent yield. The formation of **8**



33 **34**

also indicates that stabilization of the transition state by a C=C is more important in these cycloadditions than orbital overlap with the cyclopropane ring. Adduct **28,** formed with complete regiospecificity from **27,** is certainly the expected product in light of the fact that **27** not only possesses the elements of olefin **19,** but also the electronic effect of the conjugated double bond. In all cases so far encountered the latter effect exerts the predominant influence in these cycloadditions.

Based on Scheme I, there are two explanations that would satisfy the results. One involves a concerted $\pi 2_s + \pi 2_a$ pathway throughout all systems but in which electronic, stereoelectronic, or special steric effects can force process 1 → 3 to override process 2 → 4. An alternative explanation would regard the concerted $\pi 2_s + \pi 2_a$ pathway as normal but capable of being diverted into a nonconcerted or into a forbidden $\pi 2_s + \pi 2_s$ process by these special effects. We favor the first explanation because of the bulk of evidence, including stereochemical specificity[3-6] in a wide range of systems, renders nonconcertedness unlikely and because the small energy differences expected to accompany the structural changes described do not warrant a change in mechanism to what should be a higher energy forbidden process. The reversibility of the cycloaddition exhibited by **13** without concurrent formation of the more stable regioisomer **14** also renders a stepwise process unlikely.

Experimental Section

Adducts of Dichloroketene with 3,3-Dimethylcyclopentene (5). To 4.92 g (51 mmol) of the vigorously stirred olefin[8] in a 10-ml flask (fitted with a septum in which a needle connected to a nitrogen bubbler was inserted) was added portionwise via two syringes 0.95 ml (0.69 g, 6.8 mmol) of triethylamine and 0.63 ml (0.96 g, 6.5 mmol) of freshly distilled dichloroacetyl chloride. The reagents were added simultaneously at constant equimolar rates over a 3-h period. The brown mixture was allowed to stir for 17 h at room temperature. The excess olefin was distilled (bulb-to-bulb) by first cooling the reaction mixture under nitrogen with a dry ice bath, then attaching an aspirator, cooling the receiver in dry ice, removing the bath from the reaction mixture, and allowing the olefin to distill with stirring but no heating. In this manner, 3.87 g (90% of theory) of the olefin was recovered. The pot residue was thoroughly extracted with pentane, and the extracts were filtered and evaporated to 1.13 g of a brown liquid. Kugelrohr distillation at 70–100 °C (0.2 mm) gave 0.68 g (51%) of a colorless liquid. Preparative VPC[26a] provided pure samples of the two isomeric adducts.

A. 6,6-Dichloro-2,2-dimethylbicyclo[3.2.0]heptan-7-one (**7**), a white crystalline solid (29 mg) melting near room temperature: NMR (CCl_4) 9.03 (s, 3 H, *exo*-CH_3), 8.77 (s, 3 H, *endo*-CH_3), 8.4 (m, 2 H, ring CH_2), 7.8 (m, 2 H, ring CH_2), 6.66 (m, 1 H, 5-H), 6.45 (d, J = 8 Hz, 1 H, 1-H); ir 1799 (s), 1377 (m), 1395 (m), 760 (s), 688 (s), cm^{-1}. NMR shifts for addition of 12 mg of Eu(fod)$_3$ to ca. 25 mg of **7** in 0.4 ml of CCl_4: *exo*-CH_3, 5; *endo*-CH_3, 19; 5-H, 13; 1-H, 21 Hz downfield.

B. 7,7-Dichloro-2,2-dimethylbicyclo[3.2.0]heptan-6-one (**6**), a colorless liquid (116 mg): NMR 9.0 (s, 3 H, *exo*-CH_3), 8.50 (s, 3 H, *endo*-CH_3), 8.1 (m, 4 H, ring CH_2), 6.98 (d, J = 8 Hz, 1 H, 1-H), 6.03 (m, 1 H, 5-Hl); ir 1805 (s), 1377 (m), 1397 (m), 738 (s), 680 (s) cm^{-1}. NMR shifts for addition of 126 mg of Eu(fod)$_3$ to ca. 40 mg of **6** in 0.4 ml of CCl_4: *exo*-CH_3, 6; *endo*-CH_3, 9; 1-H, 18; 5-H, 31 Hz downfield.

Anal. Calcd for $C_9H_{12}Cl_2O$ (mol wt 207.1): C, 52.22; H, 5.84; Cl 34.24. Found: C, 51.98; H, 5.70; Cl, 34.41.

A mixture of the two isomers was also collected by preparative VPC and analyzed.

Anal. Calcd for $C_9H_{12}Cl_2O$ (mol wt 207.1): C, 52.22; H, 5.84; Cl, 34.24. Found: C, 52.44; H, 6.00; Cl, 34.43.

Europium NMR Shifts for Known Compounds. The following data are the downfield shifts, in Hz, for addition of the given amount of Eu(fod)$_3$ (first figure) to the given dichloroketene adduct in 0.4 ml of CCl_4.

A. 134 mg to 46 mg of 2,2-ethano-6,6-dichlorobicyclo[3.2.0]-hept-3-en-7-one (**8**): 5-H, 8; 1-H, 12; 3-H, 4; 4-H, 6.

B. 176 mg to ca. 40 mg of 3,3-dimethyl-8,8-dichlorobicyclo[4.2.0]octan-7-one (**9**): *exo*-CH_3, 2; *endo*-CH_3, 3; 1-H, 14; 6-H, 24.

C. 147 mg to ca. 40 mg of 2*a*,2*a*-dichloro-2α,3α-ethanocholestan-3*a*-one (**10**): 19-CH_3, 5; 18, 21, 26, and 27-CH_3, 0; 2-H, 11; 3-H, 21.

D. 142 mg to 44 mg of 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one (**11**): 4-*exo*-H, 14; 4-*endo*-H, 26; 1-H, 12; 5-H, 23; 2-H, 10; 3-H, 7.

E. (The shift for the following ketone was much larger than for the dichloroketene adducts.) 124 mg to ca. 0.1 g of 2α,2α-ethanocholestan-3*a*-one (**18**): 3-H, 3.24 ppm downfield.

***cis*-*N*-Benzyl-1,1-dimethyl-2-(dichloromethyl)cyclopentane-3-carboxamide (12).** To 40.8 mg (0.197 mmol) of the major isomer (**6**) from the above experiment in 0.2 ml of anhydrous ether was added 20.9 mg (0.195 mmol) of benzylamine. A precipitate slowly formed, and the mixture was allowed to stand overnight at room temperature. The ether was evaporated, and the off-white solid was washed with petroleum ether (bp 85–100 °C) to give 44 mg of a white solid: mp 116–117 °C; NMR ($CDCl_3$) 8.75 (s, 3 H, CH_3), 8.72 (s, 3 H, CH_3), 8.2 (m, 4 H), 7.53 (dd, J = 8, 10.5 Hz, 1 H, 2-H), 7.0 (m, 1 H, 3-H), 5.6 (d, J = 6 Hz, 2 H, NCH_2), 4.05 (bs, 1 H, NH), 3.66 (d, J = 10.5 Hz, 1 H, $CHCl_2$), 2.68 (s, 5 H, ArH); ir ($CHCl_3$) 3440 (m), 1670 (s) cm^{-1}; MS *m/e* 314, 316 (M), 278 (M − HCl), 242 (M − 2HCl), 230 (M − $CHCl_2$), 91 (C_7H_7).

Adducts of Diphenylketene with 5. A mixture of 0.63 g (6.6 mmol) of the olefin and 0.62 g (3.2 mmol) of diphenylketene[27] was sealed in a capillary under nitrogen at aspirator pressure and heated in a stream of steam (ca. 100 °C) for 11 days. The solution was taken up in pen-

tane and filtered through a short column of acid washed alumina with suction. The alumina was washed with 200 ml of petroleum ether (bp 60–70 °C), and the filtrate was evaporated to 0.29 g a colorless gum which appeared to be a pure mixture of the two adducts **13** and **14** in a ratio of 2.9:1 by NMR integration. Washing the alumina with 2–3% ethyl acetate in petroleum ether gave a further 0.53 g of isomers in a ratio of 11.5:1. A third wash, this time with 10% ethyl acetate in petroleum ether, yielded no further product. Thus, the total yield of adducts was 0.82 g (89%). From the ratios in the two fractions, the actual product ratio was calculated to be 5.9:1. The products were combined, and NMR integration gave a ratio of 5.5:1. The average of these ratios is 5.7:1. Recrystallization from methanol provided a 7:1 mixture in the form of a white solid.

Anal. Calcd for $C_{21}H_{22}O$ (mol wt 289.4): C, 86.85; H, 7.64. Found: C, 86.98; H, 7.74.

Preparative TLC[28a] on a small scale separated the two isomers, **13**, R_f 0.32, and **14**, R_f 0.45 (six elutions). The major isomer, **13**, melted at 84–5 °C after recrystallization from methanol.

A. 2,2-Dimethyl-7,7-diphenylbicyclo[3.2.0]heptan-6-one (**13**): NMR (CCl_4) 9.54 (s, 3 H, *endo*-CH_3), 8.98 (s, 3 H, *exo*-CH_3), 8.8–7.6 (m, 4 H, ring CH_2), 6.72 (d, J = 9 Hz, 1 H, 1-H), 6.39 (m, 1 H, 5-H), 2.82 (m, 10 H, ArH); ir 1767 cm^{-1}. NMR shifts for addition of 88 mg of Eu(fod)$_3$ to ca. 40 mg of **13** in 0.5 ml of CCl_4: *endo*-CH_3, 1.02; *exo*-CH_3, 0.67; 4-*endo*-H, 2.6; 1-H, 1.61; 5-H, 3.17; *m*- and *p*-ArH, 0.44; *o*-ArH, 2.51 ppm downfield.

Anal. Calcd for $C_{21}H_{22}O$ (mol wt 289.4): C, 86.85; H, 7.64. Found: C, 87.02; H, 7.65.

B. 2,2-Dimethyl-6,6-diphenylbicyclo[3.2.0]heptan-7-one (**14**): NMR (CCl_4) τ 9.05 (s, 3 H, *exo*-CH_3), 8.73 (s, 3 H, *endo*-CH_3), 8.8–7.6 (m, 4 H, ring CH_2), 6.79 (d, J = 7.5 Hz, 1 H, 1-H), 6.27 (m, 1 H, 5-H), 3.7 (m, 10 H, ArH); ir 1761 cm^{-1}. NMR shifts for addition of 90 mg of Eu(fod)$_3$ to ca. 30 mg of **14** in 0.4 ml of CCl_4: *exo*-CH_3, 0.56; *endo*-CH_3, 1.58; 1-H, 2.67; 5-H, 1.27; *m*- and *p*-ArH, 0.2; *o*-ArH, 1.9 ppm downfield.

Reaction of 5 with *tert*-Butylcyanoketene. A mixture of 6.36 g (67 mmol) of the olefin and 1.00 g (3.32 mmol) of 2,5-di-*tert*-butyl-3,6-diazido-*p*-benzoquinone[29] was refluxed for 1 h under nitrogen and allowed to stand at room temperature for 70 h. The excess olefin was distilled (<20 °C) at aspirator pressure into a flask at −70 °C, giving 5.46 g. The residue appeared by NMR to be mostly a 1:1 adduct, and only one isomer could be detected. Trituration with pentane precipitated a few milligrams of an off-white solid (mp >300 °C) whose NMR had the appearance of polymeric ketene. Preparative TLC[28b] provided a small amount of purified adduct, at the expense of some product loss and decomposition. As the product was manipulated over a period of time a new isomer appeared to slowly grow in minor proportion. For 2,2-dimethyl-6-*exo*-cyano-6-*endo*-*tert*-butylbicyclo[3.2.0]heptan-7-one (**15**): NMR (CCl_4) 8.95 (s, 3 H, 2-*exo*-CH_3), 8.56 (s, 3 H, 2-*endo*-CH_3), 8.75 (s, 9 H, *t*-Bu), 8.5–7.7 (m, 4 H, ring CH_2), 6.88 (d, J = 9 Hz, 1 H, 1-H), 5.93 (m, 1 H, 5-H); ir 1783, 2240 cm^{-1}. NMR shifts for addition of 36 mg of Eu(fod)$_3$ to ca. 30 mg of the adduct in 0.4 ml of CCl_4: *exo*-CH_3, 0.29; *endo*-CH_3, 0.49; *t*-Bu, 1.21; 5-H, 1.31; 1-H, 1.83 ppm downfield.

2,2-Dimethyl-6-*exo*-cyano-6-*endo*-*tert*-butylbicyclo[3.2.0]heptan-7-*endo*-ol (16). To 0.3 g of the crude product from the addition of *tert*-butylcyanoketene to 3,3-dimethylcyclopentene (0.3 g) in 3 ml of absolute ethanol was stirred for 1 h with 63 mg of sodium borohydride under nitrogen. Aqueous workup gave 0.31 g of an orange oil (five spots by TLC), and preparative TLC[28c] yielded 0.12 g of white crystalline solid, R_f 0.45, mp 109–111 °C. The other bands amounted to a total of 0.15 g, none of which appeared by NMR to be isomers of **16**. NMR ($CDCl_3$) 9.02 (s, 3 H, *exo*-CH_3), 8.92 (s, 3 H, *endo*-CH_3), 8.86 (s, 9 H, *t*-Bu), 8.7–7.9 (m, ring CH_2), 6.22 (dd, J = 9, 11 Hz, 1-H), 5.78 (dd, J = 4.5, 11 Hz, CHOH); ir ($CHCl_3$) 3600, 3460 (b), 2240, 1372 cm^{-1}; MS (*m/e*) 221 (M), 194 (M − HCN). NMR shifts for addition of 56 mg of Eu(fod)$_3$ to 32 mg of **16** in 0.4 ml of $CDCl_3$: *exo*-CH_3, 1.01; *endo*-CH_3, 1.89; *t*-Bu, 1.29 ppm downfield.

Tosylhydrazone (20). A mixture of 14.7 g (0.079 mol) of tosylhydrazine, 10.0 g (0.079 mol) of 90% pure 2,2-dimethylcyclohexanone (by NMR and GC), and 35 ml of absolute ethanol was refluxed for 2 h, allowed to cool, and placed in the refrigerator overnight. The white solid was collected and washed with a little cold ethanol. Recrystallization from absolute ethanol afforded white prisms, mp 113–4 °C (lit.[18] 129–130 °C). A second crop melted at 120–133 °C. Both crops appeared to be pure tosylhydrazone (**20**) by NMR. The yield was 16.2 g (70%). NMR ($CDCl_3$) τ 8.97 (s, 5 H, CH_3), 8.47 (m, 6 H, ring CH_2), 7.73 (m, 2 H, $CH_2C{=}N$), 7.57 (s, 3 H, $ArCH_3$), 2.67 (d, J = 8 Hz, 2 H, ArH), ca. 2.4 (b, 1 H, NH).

3,3-Dimethylcyclohexene (19). To a suspension of 94.1 g (0.32 mol) of tosylhydrazone (**20**) in 600 ml of dry ether under nitrogen, with ice bath cooling and vigorous stirring, was added 360 ml (0.75 mol) of 2.1 M methyllithium in ether (Alfa Inorganics) during 15 min. The mixture was allowed to warm to room temperature and stirred for 2.5 h. Water (500 ml) was then added, very slowly at first, and the resulting clear two-phase mixture was transferred to a separatory funnel with 100 ml of pentane, 100 ml of water, and 100 ml of pentane again. The layers were separated, and the aqueous layer was washed with 500 ml of pentane. The combined organic layers were dried over sodium sulfate, filtered, and distilled through Vigreaux columns. The pure olefin was collected at 102–106 °C, 26.3 g (75%); NMR (CCl_4) 9.04 (s, 6 H, CH_3), 7.9–8.8 (m, 6 H, ring CH_2), 4.57 (m, 2 H, vinyl H).

Adducts of Dichloroketene with 19. To 26 g (0.24 mol) of the olefin was added, with stirring under nitrogen, 1.10 ml of freshly distilled dichloroacetyl chloride and 0.15 ml of triethylamine every 15 min until 3.1 g (21 mmol) of the chloride and 2.5 g (25 mmol) of the amine had been added over a period of 5 h. The mixture was allowed to stir for 2 h and then allowed to stand at room temperature for 19 h. The excess olefin was recovered by vacuum distillation, and the residue was extracted with pentane. The mixture was filtered by suction, and the filtrate was distilled after evaporation of the solvent. The yield of straw-colored liquid, shown by NMR to contain only adducts **22** and **23**, was 2.5 g (54%). Preparative VPC[26b] separated the two adducts:

A. 2,2-Dimethyl-7,7-dichlorobicyclo[4.2.0]octan-8-one (**22**): NMR (CCl_4) 9.02 (s, 3 H, *exo*-CH_3), 8.73 (s, 3 H, *endo*-CH_3), 8.63 (m, 4 H, 3- and 4-H), 7.87 (m, 2 H, 5-H), 7.09 (m, 1 H, 6-H), 6.4 (d, J = 10 Hz, 1 H, 1-H); ir 1800 cm^{-1}. NMR shifts for addition of 122 mg of Eu(fod)$_3$ to ca. 30 mg of **22** in 0.3 ml of CCl_4: *exo*-CH_3, 3; *endo*-CH_3, 14; 6-H, 11; 1-H, 21 Hz downfield.

Anal. Calcd for $C_{10}H_{14}Cl_2O$ (mol wt 221.1): C, 54.30; H, 6.33; Cl, 32.13. Found: C, 54.27; H, 6.22; Cl, 32.16.

B. 2,2-Dimethyl-8,8-dichlorobicyclo[4.2.0]octan-7-one (**23**): NMR (CCl_4) 8.93 (s, 3 H, *exo*-CH_3), 8.58 (s, 3 H, *endo*-CH_3), 7.6–9.0 (m, 6 H, ring CH_2), 7.3 (d, J = 10 Hz, 1 H, 1-H), 6.68 (m, 1 Hl, 6-H); ir 1800 cm^{-1}. NMR shifts for addition of 69 mg of Eu(fod)$_3$ to ca. 15 mg of **23** in 0.3 ml of CCl_4: *exo*-CH_3, 6; *endo*-CH_3, 12; 1-H, 28; 6-H, 44 Hz downfield.

Anal. (see above). Found: C, 54.55; H, 6.41; Cl, 31.81.

2,2,4-Trimethyl-7,7-dichlorobicyclo[4.2.0]oct-4-en-8-one (28). To 1.8 g (12 mmol) of dichloroacetyl chloride and 1.0 g (8.2 mmol) of the diene, **27**, in 6 ml of pentane, with stirring under nitrogen, was added 1.2 g (12 mmol) of triethylamine in 4 ml of pentane during 1.8 h. After 20 h at room temperature and aqueous workup a brown oil was isolated which on *Kugelrohr* distillation gave 0.90 g (53%) of the adduct **28** [bp 93–99 °C (0.2 mm)]. An analytical sample was obtained by preparative VPC.[26c] NMR (CCl_4) τ 9.12 (s, 3 H, 2-*exo*-CH_3), 8.75 (s, 3 H, 2-*endo*-CH_3), 8.42 (bd, J = 17 Hz, 1 H, 3-*exo*-H), 8.25 (m, 3 H, 4-CH_3), 7.94 (bd, J = 17 Hz, 1 H, 3-*endo*-H), 6.68 (m, 1 H, 6-H), 6.37 (d of m, J = 9 Hz, 1 H, 1-H), 4.48 (m, 1 H, vinyl H); ir 1800 (s), 1670 (w) cm^{-1}; NMR shifts for addition of 99 mg of Eu(fod)$_3$ to ca. 40 mg of **28** in 0.4 ml of CCl_4: 2-*exo*-CH_3, 2; 2-*endo*-CH_3, 7; 4-CH_3, 3; 3-*endo*-H, 10; 6-H, 5; 1-H, 9; vinyl H, 5 Hz downfield.

Anal. Calcd for $C_{11}H_{14}Cl_2O$ (mol wt 233.1): C, 56.67; H, 6.05; Cl, 30.52. Found: C, 56.84; H, 6.11; Cl, 30.34.

***N*-Benzyl-1,5,5-trimethyl-*cis*-3-(dichloromethyl)cyclohexene-4-carboxamide (29).** The reaction was carried out with 0.105 g (0.45 mmol) of adduct **28** in 0.3 ml of ether and 0.048 g (0.45 mmol) of benzylamine. An immediate precipitate formed, with some warming. The mixture was allowed to stand for 30 min and filtered. The solid was washed with ether and shown by melting point (~250 °C) and NMR to be benzylamine hydrochloride. The filtrate was evaporated and showed ~50% unreacted starting material. Thus, the residue was taken up in 0.3 ml of ether and 0.48 g of benzylamine was added. The mixture was allowed to stand for 20 h. Preparative TLC[28d] gave 66 mg of a gum (R_f 0.15) whose mass spectrum showed a molecular ion at *m/e* 339 (calcd: 339). Recrystallization from ether gave **29** as off-white crystals: NMR ($CDCl_3$) τ 9.0 (s, 3 H, CH_3), 8.96 (s, 3 H, CH_3), 8.67 (m, 1 H, 6-H), 8.25 (m, 3 H, 1-CH_3), 7.88 (m, 1 H, 6-H), 7.58 (bd, J = 6 Hz, 1 H, 4-H), 7.11 (m, 1 H, 3-H), 5.58 (bd, J = 5 Hz, 2

H, NCH_2), 4.37 (m, 1 H, vinyl H), 4.34 (d, J = 10 Hz, 1 H, $CHCl_2$), 4.1 (bs, 1 H, NH), 2.67 (m, 5 H, ArH); ir ($CHCl_3$) 3440, 3395, 1660, 1382, 1373, 910 cm^{-1}.

***N*-Benzyl-*cis*-2-(dichloromethyl)-5,5-dimethylene-3-cyclopentene-1-carboxamide (26).** The dichloroketone **8**[21] (1 g, 5 mmol) in 3 ml of ether was treated with 0.53 g (5 mmol) of benzylamine for 30 min. A quantitative yield of amide **26,** mp 138–140 °C, was obtained: NMR (Me_2SO-d_6) τ 9.1–9.5 (m, 4 H), 7.05 (d, J = 8 Hz, 1 H, 1-H), 6.15 (m, 1 H), 5.73 (d, J = 5.5 Hz, 2 H, CH_2Ph), 4.34 (d of d, 1 H), 4.53 (d of d, 1 H), 3.6 (d, J = 10 Hz, 1 H, $CHCl_2$), 2.71 (m, 5 H), 1.7 (br, NH); ir (CCl_4) 1630 cm^{-1}. Anal. Calcd for $C_{16}H_{17}ONCl_2$: C, 62.0; H, 5.48. Found: C, 61.81; H, 5.31.

Zinc Reduction of 8. A mixture of 1.2 g of **8,** 0.5 g of zinc dust (activated by treatment with 10% HCl), and 1 g of glacial acetic acid in 30 ml of ether was stirred for 4 days. Workup yielded an oil which by NMR consisted mainly of monochloroketone **25a:** τ 8.6–9.5 (m, 4 H), 6.72 (d of d, J = 7 Hz and 3 Hz, 1 H, CHC=O), 5.93 (m, 1 H), 4.98 (d of d, J = 8.5 Hz and 3 Hz, 1 H, CHCl), 4.3 (d of d, J = 5.5 and 2 Hz, 1 H), 4.5 (d of d, J = 5.5 Hz, 1 H); ir 1782 cm^{-1}.

Further reduction with zinc led to a mixture of **25a** and **25b,** ir 1770 and 1785 cm^{-1}.

Acknowledgment. Support of this work by a grant from the National Science Foundation and the National Cancer Institute is gratefully acknowledged.

References and Notes

(1) (a) Cycloadditions. 22. For the previous paper in this series, see A. Hassner, D. Tang, and J. Keogh, *J. Org. Chem.,* **40,** 2102 (1976). (b) Work performed in part at the University of Colorado, Boulder, Colo.
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(28) Silica gel PF-254, 20 × 20 cm × 2 mm. Eluting solvents: (a) 99/1 Skellysolve B/ethyl acetate; (b) 6× with 99/1 ethyl acetate/Skellysolve B and 1× with 95/5; (c) 1/1 chloroform/ethyl acetate; (d) chloroform.
(29) Prepared by A. Miller in our laboratory.

The Stereochemistry of the Intramolecular Reactions of Cyclopropylcarbenes[1]

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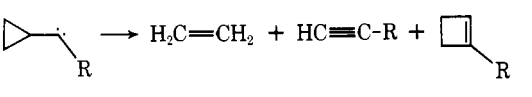
Abstract: The direct irradiation of the *cis*-dimethylcyclopropyl diazo ester (**6**) gives *cis*-2-butene, *cis*-3,4-dimethyl-1-carbomethoxycyclobutene, and methyl propiolate. The trans diazo ester (**6a**) behaves similarly. Thus both the ring expansion and fragmentation reactions proceed with retention of stereochemistry. The benzophenone- or fluorenone-sensitized decompositions also lead to retention of stereochemistry to a very high degree. A number of explanations for the observed retention are put forward. The addition of 2,3-dimethylcyclopropylcarbomethoxycarbene (**9**) to isobutylene is also discussed.

Despite many previous investigations[2,3] and wide use in synthesis,[4-6] the ring-expansion and fragmentation reactions of cyclopropylcarbenes are still imperfectly understood, and several problems are outstanding. Thus, although gas-phase reactions show relatively more fragmentation than their solution counterparts, the introduction of an inert moderator into the gas-phase reaction is sometimes without effect.[7] In unsymmetrically substituted cyclopropylcarbenes it is the less-substituted and, therefore, stronger bond that migrates in the ring expansion. This is curious, although an explanation based



upon steric effects has been put forward[8,9] and electronic factors briefly investigated as well.[10] A third puzzling aspect is the absence of the products of hydrogen migration where they might well be expected to be major products.[11-13] Other seemingly anomalous reactions continue to appear.[14]

Obviously, knowledge of the mechanism of the rearrangement is central to an understanding of the problems mentioned