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Stereodirecting Effects in the Characterization of Ylide Intermediates in Reactions of Singlet Methylene with an Allylic Ether and an Allylic Chloride

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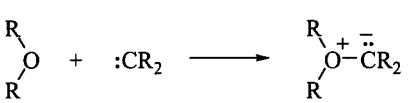
Abstract: The stereodirecting effects of substrate substituents were examined in addition of ^{1}:CH_2 to the double bonds of 3-methoxycyclohexene (**3a**), 3-chlorocyclohexene (**3b**), and 3-methylcyclohexene (**3c**) in pentane solution at temperatures from 23°C to -50°C. A preference for addition syn to the directing substituent was observed in reactions of **3a** and **3b** and was attributed to a reversible interaction of carbene and substituent. In the reaction with **3a** this interaction was not obviously ylide formation. © 1997 Elsevier Science Ltd.

INTRODUCTION

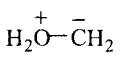
Formation of oxonium ylides in reactions of singlet carbenes or carbenoid reagents with ethers and alcohols (eq 1) has been clearly demonstrated in numerous product studies.[1] Whether or not the carbene fragment might subsequently be released from the ylide intermediate is less certain. This is uncertain, in part, because methods for preparation of oxonium ylides which do not employ carbenes or carbenoid reagents are not generally available.[2] Neither have these ylides proved suitable for study by spectroscopic methods.[3] A number of reports of reversible ylide formation in reactions of carbenes with alcohols have appeared based on kinetic and isotope effect studies employing several carbenes, including diphenylcarbene and fluorenylidene.[4] Platz and Maloney have critically reviewed this work and have offered alternate interpretations of the experimental data.[3a] Although there is certainly very strong evidence supporting the formation of carbene-ether adducts capable of undergoing intramolecular rearrangements typical of ylides, retention of carbene-like reactivity by carbene-ether adducts has also been invoked to explain experimental observations. For example, Tomioka et al. studied the effect of several ether solvents on the insertion of arylcarbenes into the O-H bonds of alcohols and reported that the solvent 1,4-dioxane had a significant effect on the selectivity of these carbenes.[5] They attributed this effect to formation of a complex between arylcarbene and 1,4-dioxane solvent.



(1)

Computational studies point to a low binding energy for oxonium methylide (**1**).[6] A recent study by Gonzalez et al. at the QCISD(T)/6-311++G**//QCISD/6-311++G** level of theory predicts a 6.4 kcal/mol

barrier for dissociation of **1** to ^{1}:CH_2 and H_2O and describes the ylide as "a long-range complex between water and singlet methylene where the geometries of the two moieties do not change considerably".[6e] The study indicates that solvation may significantly effect barriers to ylide rearrangement. Earlier calculations performed by Moreno et al. at the HF/3-21G level suggest that the carbene fragment may be transferred from **1** to ethylene to form cyclopropane in a concerted process; that is the ylide may act as a solvated carbene.[7]



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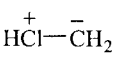
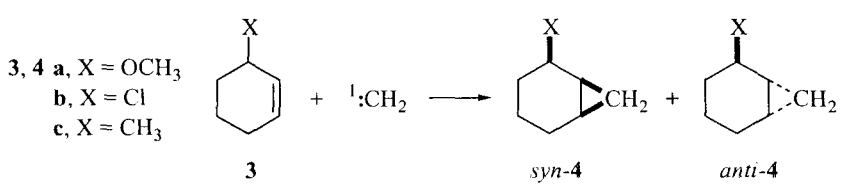


2

An even smaller binding energy than that predicted for **1** was calculated by Yates et al. for chloronium methylide (**2**).[6c] At the MP4/6-311G(df,p) level the binding energy was predicted to be 4 kcal/mol (Calculations at this level predict a binding energy of 12 kcal/mol for **1**.[6c]). Products consistent with the formation of ylide intermediates have been observed in the reactions of chlorinated substrates with various carbenes.[1] However, there is evidence that these products might be formed by a single electron transfer mechanism, bypassing ylide intermediates.[8] If ylides are formed in these reactions, then questions concerning their ability to release the carbene would certainly be very reasonable.

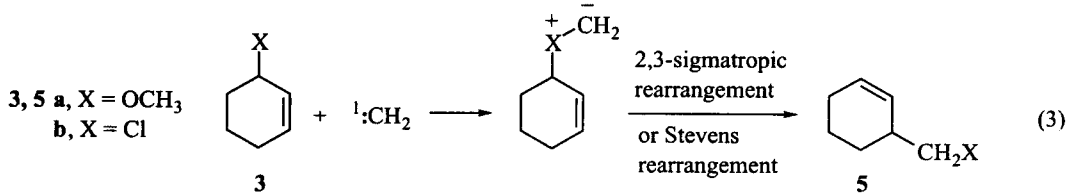
In an earlier study we examined the effects of substrate methyl, hydroxy, methoxy, and methylthio groups on the stereochemistry of ^{1}:CH_2 addition to a double bond (eq 2), with the expectation that reversible complexation of the carbene by the substrate functional group might direct the carbene to the proximate face of the double bond.[9] The intervention of an ylide or functional group-carbene adduct in a directed attack would require that either: (1) the adduct behave as a carbenoid species, or (2) the formation of the adduct be reversible, with capture of the carbene by the proximate face of the double bond following its release from the directing group.



3 *syn*-**4** *anti*-**4** (2)

Singlet methylene reacts at nearly diffusion controlled rates and is notoriously unselective.[10] In spite of this, the product ratio *syn*-**4**/*anti*-**4** did vary from a predicted statistical ratio of one. Only in the reaction of 3-methoxycyclohexene (**3a**) did the substituent promote cyclo-propanation of the *syn*-face of the double bond (*syn*-**4a**/*anti*-**4a**, 1.14 ± 0.02) and this was attributed to a through-space interaction with the carbene. The stereochemical preference was solvent-dependent; a small preference for formation of *anti*-**4a** was observed when the reaction was run in ether solution (*syn*-**4a**/*anti*-**4a**, 0.92 ± 0.03), consistent with competing

complexation of carbene by solvent. Formation of product **5a** in this reaction provided evidence for formation of an oxonium ylide (eq 3).



(3)

Comparison of results obtained in similar experiments with dichlorocarbene vs ^{1}:CH_2 support a through-space rather than a through-bond interaction as the source of the directing effect. Dichlorocarbene is considerably more discriminating than ^{1}:CH_2 in reactions with alkenes.[10] If a through-bond interaction of the methoxy group with the substrate double bond was the source of the directing effect, then a more pronounced directing effect might be expected in reactions of dichlorocarbene with **3a**. Instead, the reaction of dichlorocarbene with **3a** leads to predominantly the *anti*-isomer of the cyclopropanated product.[11]

In work reported here, the very low binding energy predicted for chloronium ylide **2**[6c] prompted us to look for a similar directing effect in the reaction between ^{1}:CH_2 and 3-chlorocyclohexene (**3b**). Experiments were also carried out at less than ambient temperatures with substrate **3a**, **3b**, and 3-methylcyclohexene (**3c**). The results of these experiments are consistent with a through-space interaction between the carbene and directing substituent in at least some fraction of reactions leading to cyclopropanation of the *syn*-face of the double bond of **3a** and **3b**. However, experiments with **3a** bearing on detection and trapping of the ylide intermediate indicate that the ylide is not obviously involved as an intermediate in this process.

RESULTS AND DISCUSSION

Directing Effect of a Chloro Substituent

Reactions were carried out between chlorine-bearing substrate **3b** and ^{1}:CH_2. The carbene was generated by photolysis of diazirene, prepared using the method of Ohme and Schmitz.[12] Diazirene was used as the carbene precursor in these experiments, as opposed to diazomethane, because of its greater stability towards the radicals which may be generated in reaction of ^{1}:CH_2 with chlorinated compounds.[13] Diazirene was transferred to 5 mL of a 5% solution of **3b** in dry solvent. Solutions were photolyzed, under N_2, using a Canrad-Hanovia 450-W mercury lamp held in a Pyrex immersion well. Solution temperatures of approximately 23°C were maintained by contact of the solution with a tap water-cooled cold finger. A deficient amount of diazirene was used; less than 5% of the substrate underwent reaction. Reaction mixtures were analyzed by capillary GC immediately upon completion of photolysis.

The carbene reacted by insertion into C-H bonds of substrate and solvent, as well as by attack at the substrate double bond and chlorine atom, leading to complex reaction mixtures. Cyclopropanated products

syn-**4b** and *anti*-**4b** were identified in the reaction mixture by comparison with authentic samples (GC coinjection and GC/MS). An authentic sample containing predominantly *syn*-**4b** was prepared by reaction of *syn*-bicyclo[4.1.0]heptan-2-ol with chlorotrimethylsilane in CH_2Cl_2. A sample containing predominantly *anti*-**4b** was prepared by reaction of *syn*-bicyclo[4.1.0]heptan-2-ol with triphenylphosphine and hexachloroacetone. Product **5b**,[14] formed by attack of the carbene on the chlorine atom (eq 3), was identified by comparison with a sample prepared by treatment of the corresponding alcohol with triphenylphosphine and pyridine in CCl_4. A number of other products were observed in the photolysis mixtures, but not identified. These were assumed to be the anticipated products of C-H insertion,[10] consistent with analysis of the product mixtures by GC/MS. The relatively labile bicyclic products appeared to rearrange upon standing to give 4-chlorocycloheptene.[14,15] However, 4-chlorocycloheptene was not present in the product mixtures when analyzed within hours of photolysis. GC response factors were not measured, but assumed to be equal for pairs of isomers. This assumption was supported by close agreement between product ratios determined by GC and by ^{1}H NMR spectroscopy for synthetic mixtures.

Product ratios are reported in Table 1. When the reaction was run in pentane solution at 23°C the ratio *syn*-**4b**/*anti*-**4b** was 1.01 and the ratio **5b**/*anti*-**4b** was 2.77. Both ratios were significantly smaller when the reaction was run in ether solution. The reaction was repeated in pentane solution at several temperatures ranging from 0°C to -50°C in hopes that a preference for addition to the *syn*-face of the double bond would be observed. We reasoned that lower temperatures would favor a reversibly formed intermediate ylide or complex. If both the reversibly formed intermediate and the activation barrier leading from the intermediate to product *syn*-**4b** were lower in energy than the starting materials, then the reaction would have a negative energy of activation, i.e., would be faster at lower temperatures.[16] In fact, the ratio *syn*-**4b**/*anti*-**4b** was greater in reactions run at lower temperatures, with a value of 1.48 at -50°C. There was a corresponding increase in the ratio **5b**/*anti*-**4b**.

The temperature dependence observed in the reaction of ^{1}:CH_2 with **3b** stands in contrast to the lack of temperature dependence reported for product distributions in reactions of ^{1}:CH_2 with alkane substrates. In 1956 Doering et al. reported that the distributions of products in reactions of pentane with ^{1}:CH_2 at -75°C vs 15°C were virtually identical,[17] as would be expected for competing diffusion controlled processes. Because we can only infer *relative* rates in the reaction of ^{1}:CH_2 with **3b**, we do not know whether the rates for the reactions leading to both cyclopropanated products are slower at the lower temperature, but the reaction leading to *syn*-**4b** has been slowed to a lesser degree; or whether the process leading to *syn*-**4b** is actually faster at the lower temperature than it was at room temperature, indicating a negative energy of activation. However, because the rates of the two processes depend differently on temperature, we do conclude that the rate of at least one of these reactions is probably not simply diffusion controlled.

*Temperature Dependence of Product Ratios in Reactions of **3a** and **3c***

In order to characterize the temperature dependence of the directing effect observed earlier in experiments with substrate **3a**,[9] the stereochemistry of ^{1}:CH_2 addition to the double bonds of substrates **3a**

Table 1. Product Ratios from Reactions of ^{1}:CH_2 with **3a-c**

substrate	precursor	solvent	temp, °C	*syn*-**4**/*anti*-**4**[a]	**5**/*anti*-**4**[a]
3a	diazomethane	pentane	18[b]	1.15	1.62
3a	diazirene	pentane	23	1.30 (0.02)	1.07 (0.02)
3a	**6**	pentane	23	1.18 (0.02)	2.22 (0.02)
3a	diazomethane	pentane	23[c]	1.14 (0.02)	1.59 (0.07)
3a	diazomethane	pentane	11	1.18	1.61
3a	diazomethane	pentane	-8	1.28	1.99
3a	diazomethane	pentane	-25	1.41	2.59
3a	diazomethane	pentane	-37	1.51	2.84
3a	diazomethane	pentane	-50	1.67	3.28
3a	diazomethane	pentane/2.4% *t*-BuOH	18	1.14 (0.04)	1.01 (0.12)
3a	diazomethane	pentane/2.4% *t*-BuOH	-50	1.63 (0.01)	2.53 (0.03)
3a	diazomethane	pentane/9.1% *t*-BuOH	18	1.08 (0.02)	0.80 (0.03)
3a	diazomethane	ether	23[c]	0.92 (0.03)	1.30 (0.05)
3b	diazirene	pentane	23	1.01 (0.02)	2.77 (0.17)
3b	diazirene	pentane	0	1.10	2.85
3b	diazirene	pentane	-20	1.28	3.38
3b	diazirene	pentane	-35	1.36	3.90
3b	diazirene	pentane	-50	1.48	4.03
3b	diazirene	ether	23	0.84 (0.01)	2.37 (0.06)
3c	diazomethane	pentane	23[c]	0.95 (0.02)	
3c	diazomethane	pentane	11	0.96	
3c	diazomethane	pentane	-8	0.97	
3c	diazomethane	pentane	-25	0.97	
3c	diazomethane	pentane	-37	0.98	
3c	diazomethane	pentane	-50	0.98	
3c	diazomethane	ether	23[c]	0.95 (0.01)	

[a]Standard deviations are reported in parentheses following mean value from three reactions (GC analysis). Where standard deviations are not reported, the ratio is from a single reaction. [b]Calculated using Arrhenius equation. [c]Ref 9.

and **3c** was determined at six temperatures ranging from 23°C to -50°C. Diazomethane was transferred to 5 mL of a 4% solution of substrate in dry pentane. Solutions were photolyzed as described above. Products were identified and product ratios determined as described previously.[9] Product ratios are reported in Table 1. There was no significant difference between the ratios *syn*-**4c**/*anti*-**4c** produced in the reaction with methyl-bearing substrate **3c** at 23°C vs -50°C. In contrast, in reactions with ether **3a** there was a pronounced increase in product ratios *syn*-**4a**/*anti*-**4a** and **5a**/*anti*-**5a** at lower temperatures, paralleling the results obtained with chlorine-bearing substrate **3b**.

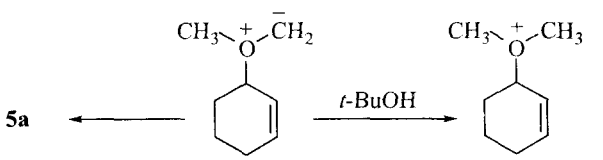
Arrhenius plots for reactions with substrates **3a-c** are shown in Figures 1 and 2. The differences in activation parameters for the formation of pairs of products, shown in Table 2, are calculated according to the formula

$$\text{product A/product B} = k_A/k_B = \exp(\Delta\Delta S^{\ddagger}/R)\exp(-\Delta\Delta H^{\ddagger}/RT)$$

In reactions of **3a** and **3b**, both enthalpies and entropies of activation for formation of the *syn*-isomers of the bicyclic products are less than those for the formation of the *anti*-isomers, consistent with a through-space stabilizing interaction between the nucleophilic substituents and the carbene, and with a more structured transition state. A similar trend is seen when comparing formation of products **5a** and **5b**, arising from carbene attack at the substituent, with cyclopropanation of the anti face of the double bond. In contrast, activation parameters for formation of *syn*-**4c** vs *anti*-**4c** in reaction with methyl-bearing substrate **3c** are very similar.

Effect of Proton Donor on Product Stereochemistry

Kirmse et al. have shown that oxonium methylides formed by reaction of ^{1}:CH_2 with oxetane can be readily protonated.[18] We reasoned that in the reaction of ^{1}:CH_2 with ether **3a** a proton donor might be used to "trap" an ylide intermediate in competition with intramolecular rearrangement to product **5a** (eq 4). If the oxonium ylide was also the intermediate involved in the formation of excess *syn*-**4a**, then protonation would lead to a corresponding decrease in the *syn*-**4a**/*anti*-**4a** ratio.



(4)

Pentane solutions containing 2.4% **3a**, 2.4% *t*-butanol, and diazomethane were photolyzed at both 18°C and -50°C and product mixtures analyzed as before. Results are shown in Table 1. The presence of the proton donor had a significant impact on the ratio **5a**/*anti*-**4a**. At 18°C this ratio decreased from 1.62 in dry pentane to 1.01 with the addition of *t*-butanol. At -50°C, the ratio dropped from 3.28 to 2.53. In contrast, the presence of the proton donor had no detectable effect on the *syn*-**4a**/*anti*-**4a** ratio at either 18°C or -50°C. Increasing the *t*-butanol concentration to 9.1% at 18°C resulted in a further decrease in the **5a**/*anti*-**4a** ratio to

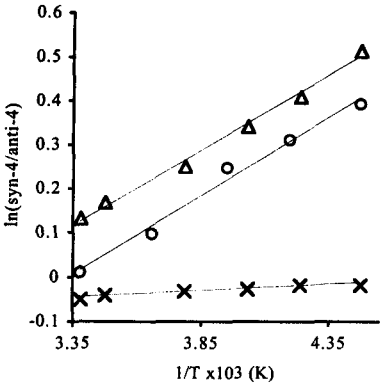


Figure 1. Arrhenius plot for product ratios *syn*-**4a**/*anti*-**4a** (Δ), *syn*-**4b**/*anti*-**4b** (O), and *syn*-**4c**/*anti*-**4c** (X).

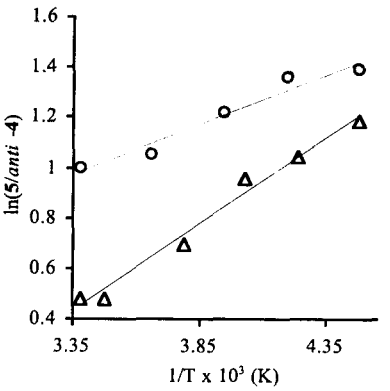


Figure 2. Arrhenius plot for product ratios **5a**/*anti*-**4a** (Δ) and **5b**/*anti*-**4b** (O).

Table 2. Activation Parameter Differences for Formation of Pairs of Products in Reactions of ^{1}:CH_2 with **3a-c**

substrate	product A/ product B	$\Delta S^{\ddagger}_A - \Delta S^{\ddagger}_B$, cal/mol·K[a]	$\Delta H^{\ddagger}_A - \Delta H^{\ddagger}_B$, kcal/mol[a]
3a	*syn*-**4a**/*anti*-**4a**	-2.0 (0.1)	-0.68 (0.03)
3a	**5a**/*anti*-**4a**	-3.8 (0.4)	-1.4 (0.1)
3b	*syn*-**4b**/*anti*-**4b**	-2.4 (0.2)	-0.71 (0.05)
3b	**5b**/*anti*-**4b**	-0.71 (0.40)	-0.79 (0.10)
3c	*syn*-**4c**/*anti*-**4c**	-0.31 (0.03)	-0.064 (0.01)

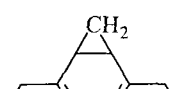
[a]Standard errors are shown in parentheses.

0.80 and a corresponding decrease in the *syn*-**4a**/*anti*-**4a** ratio from 1.15 in dry pentane to 1.08. We are hesitant, however, to conclude that this apparent change in stereochemistry at the higher *t*-butanol concentration is due to protonation of a common ylide intermediate. We are hesitant because ether solvent also effects the *syn*-**4a**/*anti*-**4a** ratio, probably through competing solvation of the carbene or increased solvent polarity.[9] It is possible that the effect of ether solvent and the effect of the higher *t*-butanol concentration on the *syn*-**4a**/*anti*-**4a** ratio have the same origin. While ether solvent also effects the **5a**/*anti*-**4a** ratio, the effect is smaller than that produced by addition of *t*-butanol. We conclude that formation of **5a** and excess *syn*-**4a** are not *obviously* linked by a common intermediate.

Comparison of Different Carbene Precursors

The results of all of the experiments described above might be explained by an interaction between the carbene precursor, rather than carbene, and the directing group. This possibility was tested by irradiating solutions of ether **3a** with three different precursors known to produce ^{1}:CH_2: diazomethane (eq 5), diazirene (eq 6), and hydrocarbon **6** (eq 7).[19] Results are shown in Table 1.

$$N_2CH_2 \xrightarrow{h\nu} N_2 + {}^1{:}CH_2 \qquad (5)$$



(6)

(7)

6

A directing effect was observed in reactions with all three precursors, however there were reproducible differences in the *syn*-**4a**/*anti*-**4a** ratios observed with diazirene (1.30) vs diazomethane (1.18) or **6** (1.14). At least one of the precursors does appear to be involved in reactions leading to the cyclopropanated products. However, because a directing effect was observed in all three cases, and particularly because of the similarity between results obtained with diazomethane and with **6**, we believe that the free carbene must be responsible, at least to large extent, for the directing effect. Still larger differences were seen between ratios **5a**/*anti*-**4a** obtained in reactions employing different precursors, but these differences are quite likely due to protonation of the ylide intermediate by varying amounts of adventitious water. Indeed, when the photolysis of **3a** with **6** was repeated in pentane that was deliberately saturated with water the ratio **5a**/*anti*-**4a** dropped to 1.36 (vs 2.22 in dry pentane) and the *syn*-**4a**/*anti*-**4a** ratio was 1.18.

Interaction between the Methoxy Substituent of ***5a*** *and* ^{1}:CH_2

We suggest three possible explanations for the directing effect observed in reactions of ^{1}:CH_2 with **3a**:

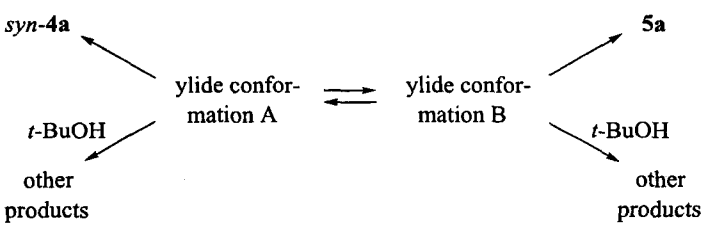
(1) Two (or more) kinetically distinct conformations of the ylide may exist (ylide conformations A and B, Scheme 1). To accomodate the observations, conversion of conformation A to *syn*-**4a** would have to be faster than its protonation by *t*-butanol. This might be reasonable for a conformation in which the carbene fragment is situated over the double bond. Protonation and/or rearrangement of conformation B would have to be faster than conversion to conformation A.

(2) A reversibly formed carbene-substrate contact pair may be responsible for the directing effect (Scheme 2). This contact pair would be the immediate precursor to both the excess *syn*-**4a** and the ylide which rearranges to **5a**. The contact pair would be protected from dissociation by barriers to diffusion, as well as by stabilizing dipole-dipole interactions between the carbene and the substrate substituent. The contact pair may be protected from product formation by very small, possibly entirely entropic, barriers.

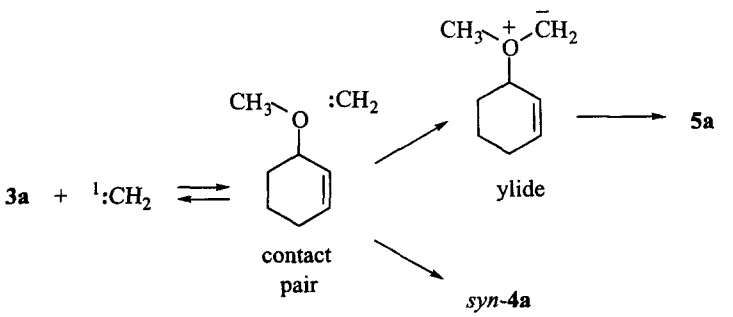
(3) Diffusion towards the syn-face of the double bond may be assisted by long range dipole-dipole interactions between the carbene and the substrate substituent.[20] Using ab initio calculations, Gonzalez et al. predicted the dipole moment for ^{1}:CH_2 to be 2.11 D,[6e] comparable to the dipole moment for H_2O. Mechanism 3 may operate alone, or in combination with mechanism 1 or 2.

Note that in all three cases the directing effect may be diminished in the presence of a more polar or nucleophilic solvent, as was actually observed.

Scheme 1



Scheme 2



Conclusions

A preference for addition of ^{1}:CH_2 to the face of the double bond proximate to the substrate chloro substituent has been observed in reactions of **3b** carried out below room temperature. This result parallels

results obtained with ether **3a**. In both cases the preference for addition syn to the substituent is more pronounced at lower temperatures and absent in ether solution. In contrast, reactions with methyl-bearing substrate **3c** show no temperature or solvent dependence. Further experiments indicate that, at least in reactions with **3a**, that the directing effect is probably not due solely to an interaction between the carbene precursor and the substrate substituent. The formation of product **5a** in reactions with **3a** is attributed to rearrangement of an ylide formed by attack of ^{1}:CH_2 on the oxygen atom of the methoxy substituent. Addition of *t*-butanol significantly decreases the yield of **5a**, presumably as a result of protonation of the ylide intermediate, but has a less obvious effect, if any, on the stereochemistry of carbene addition to the double bond. Possible explanations for the directing effect include the transfer of methylene to the syn face of the double bond from certain conformation(s) of an ylide intermediate, intervention of a carbene-substrate contact pair as a key intermediate, and diffusion assisted by long range dipole-dipole interactions between the carbene and substituent. Although the data does not allow a choice to be made between these possibilities, they all do involve a specific reversible interaction of the carbene with the directing group.

EXPERIMENTAL SECTION

General Remarks

^{1}H NMR spectra of $CDCl_3$ solutions were recorded on a Varian Gemini 300 MHz spectrometer and referenced to the solvent peak. Mass spectra were obtained on a Hewlett-Packard 5970 Series quadrupole mass detector connected to a Hewlett-Packard 5890 GC fitted with a polydimethylsiloxane/fused silica capillary column, 25 m x 0.25 mm, 0.25μm film thickness. Capillary GC analyses were performed on a Hewlett-Packard 5890 GC with FID and SGE BPX5 column, 25 m x 0.22 mm, 0.25 μm film thickness. GC response factors for isomers were assumed identical. Reaction products were identified by comparison of GC retention times (coinjection) and by matching mass spectra with those of authentic samples.

Photolysis of Diazomethane Solutions

(*Warning!* All operations involving diazomethane should be carried out in an efficient fume hood and behind a safety shield.) Diazomethane was transferred in a stream of N_2 from a decalin solution[9] to a N_2-purged 4-5% solution of substrate in dry solvent (5 mL) in a Pyrex vessel. The solutions, under N_2, were irradiated 45 min with a Canrad-Hanovia 450-W mercury lamp held in a water-cooled, vacuum-jacketed Pyrex immersion well. During irradiation solutions were cooled either by contact with a tap water-cooled cold finger or by immersion in a cold bath. An ice-water bath was used when reactions were carried out at 0°C, a cyclohexane-liquid N_2 slush bath was used for reactions at 7°C, and an ethylene glycol-dry ice slush bath was used for reactions at -11°C. A CH_2Cl_2 bath cooled by a Neslab CC-100 II immersion cooler regulated by a Neslab Exatrol temperature controller was used when reactions were carried out at temperatures from -20 to -50°C (temperature control ± 0.1°).

Photolysis of Diazirene Solutions

(*Warning!* All operations involving diazirene should be carried out in an efficient fume hood and behind a safety shield.) Diazirene was prepared by the method of Olme and Schmitz[12] and transferred to a N_2-purged 4-5% solution of substrate in dry solvent (5 mL) in a Pyrex vessel. Solutions were irradiated using the procedure described above for solutions of diazomethane.

Photolysis of 9,10-Dihydro-9,10-methanophenanthrene (6) Solutions

Solutions of **6** (0.030 g),[19] **3a** (0.10 g) and dry pentane (1.0 mL) were irradiated 10 h, under N_2, using the procedure described above for solutions of diazomethane.

syn-2-Chlorobicyclo[4.1.0]heptane (syn-4b)

Chlorotrimethylsilane (0.15 mL, 2.0 mmol) was added dropwise to a solution of *syn*-bicyclo[4.1.0]heptan-2-ol (0.10 g, 0.89 mmol) in dry CH_2Cl_2 (2 mL) under N_2. The mixture was stirred 1.5 h at 30°C. The solvent was removed under reduced pressure, leaving a mixture of *syn*-**4b**, *anti*-**4b**, 4-chlorocycloheptene, and **5b** in the ratio 4: 1: 1: trace. Spectral data for *syn*-**4b**:[21] ^{1}H NMR ($CDCl_3$) δ 4.61 (m, 1H), 1.80-1.95 (m, 2H), 1.05-1.60 (m, 6H), 0.79 (dt, J = 4.6, 9.0 Hz, 1H), 0.46 (q, 1H, J = 5.5 Hz); MS, *m/e* (rel inten) 95 (100), 81 (16), 79 (54), 77 (20), 68 (23), 67 (65), 55 (23), 54 (27), 53 (32), 41 (45), 39 (77).

anti-2-Chlorobicyclo[4.1.0]heptane (anti-4b)

A slurry of hexachloroacetone (1.59 g, 6.02 mmol) and triphenylphosphine (0.25 g, 0.96 mmol) was cooled to 15°C under N_2. *syn*-Bicyclo[4.1.0]heptan-2-ol (0.10 g, 0.89 mmol) was added dropwise to the stirred slurry, maintaining a temperature below 20°C. The reaction mixture was stirred 3 h at room temperature. Vacuum transfer (35°C, 0.2 mm Hg) of the volatile components led to a mixture of *anti*-**4b**, *syn*-**4b**, and **5b** in the ration 4.0: 1.3: 1.1. Spectral data for *anti*-**4b**:[21] ^{1}H NMR ($CDCl_3$) δ 4.51 (m, 1H), 1.84-2.05 (m, 2H), 1.04-1.80 (m, 6H), 0.73 (dt, J = 9.1, 4.7 Hz, 1H), 0.10 (q, J = 5.3 Hz, 1H); MS, *m/e* (rel inten) 95 (71), 94 (32), 79 (100), 77 (31), 67 (81), 54 (44), 53 (44), 41 (55), 39 (98).

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