flask consisted of 30 mg of a dark, tarry product.

Based on the above reported material balances and GLC analyses, the following overall distribution has been calculated for the products derived from the C_2 moiety of **2a**: 70% of **4a**, 1% of **4b**, 2% of **4c**, 10% of **4d**, 16% of **6** and 1% of **7**.

The identification of the above described reaction products is based on the identity of the analytical data presented below for each compound with those of the corresponding authentic product:

Chloro(methylthio)acetaldehyde (4a): colorless liquid; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.15 (s, 3 H), 5.32 (d, J = 1.83 Hz, 1 H), 9.28 (d, J = 1.83 Hz, 1 H); IR (film) 1728 cm^{-1} (C=O); MS, m/e (relative intensity) 126, 124 (17, 45, M^+), 97, 95 [38, 100 $(M - CHO)^+$], 89 [27, $(M - Cl)^+$]; t_R = 14.4 min.

Synthesis of 4a. To a solution of 0.90 g (10 mmol) of **4b**[6] in 50 mL of dichloromethane a solution of 1.35 g (10 mmol) of sulfuryl chloride in 20 mL of dichloromethane was added dropwise with stirring at −15 °C to −20 °C during a period of ca. 2 h. Then the solvent was removed in a rotary evaporator at room temperature and 20 torr, and the residue was distilled at vacuum through a 5-cm unpacked column to give 1.15 g (93%) of **4a**: bp 53 °C/10 torr.

(Methylthio)acetaldehyde (4b): MS, m/e (relative intensity) 90 (60, M^+), 61 [100, $(M - CHO)^+$]; t_R = 8.3 min. Authentic sample prepared according to ref 6.

Dichloro(methylthio)acetaldehyde (4c): GC/MS, m/e (relative intensity) 162, 160, 158 (5, 24, 33, M^+), 133, 131, 129 [14, 73, 100, $(M - CHO)^+$], 125, 123 [21, 58, $(M - Cl)^+$]; t_R = 12.8 min.

Synthesis of 4c. To a solution of 1.35 g (15 mmol) of **4b** in 40 mL of dichloromethane a solution of 4.05 g (30 mmol) of sulfuryl chloride in 10 mL of dichloromethane was added with stirring at 0 °C during a period of 15 min. Stirring was continued for 30 min at 0 °C and for 1 h at room temperature, the solvent was removed in a rotary evaporator at room temperature and 15 torr, and the residue was distilled at vacuum through a 5-cm unpacked column to give 1.60 g (68%) of **4c**: bp 58 °C/16 torr; ^1H NMR ($CDCl_3$, Me_4Si): 2.27 (s, 3 H), 8.94 (s, 1 H); IR (film) 1740 cm^{-1} (C=O).

Anal. Calcd for $C_3H_4Cl_2OS$: C, 22.66; H, 2.54; Cl, 44.59; S, 20.16. Found: C, 22.79; H, 2.59; Cl, 44.43; S, 20.07.

Bis(methylthio)acetaldehyde (4d): colorless liquid; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.10 (s, 6 H), 4.25 (d, J = 2.93 Hz, 1 H), 9.28 (d, J = 2.93 Hz, 1 H); IR (film) 1710 cm^{-1} (C=O); MS, m/e (relative intensity) 138, 136 (1, 9, M^+), 107 [100, $(M - CHO)^+$]; t_R = 20.9 min.

Synthesis of 4d. To a solution of 4.65 g (65 mmol) of sodium methanethiolate in 55 mL of methanol a solution of 3.36 g (10 mmol) of **1**[11] in 5 mL of methanol was added with stirring at 0 °C during a period of 15 min. Stirring was continued for 24 h at room temperature, sodium chloride was filtered off, and the filtrate was concentrated by distillation through a rotary evaporator at room temperature and 20 torr. The liquid residue was dissolved in 25 mL of dichloromethane, sequentially washed with 100 mL of 1% hydrochloric acid, aqueous sodium bicarbonate, and water, dried over sodium sulfate, and concentrated by removal of dichloromethane in a rotary evaporator. The residue (3.40 g) was purified by chromatography (column 2 × 60 cm; 75 g of silica gel; 1200 mL of n-pentane and diethyl ether in a volumetric ratio of 95:7) to give 2.1 g (51%) of **4d**.

Anal. Calcd for $C_4H_8OS_2$: C, 35.27; H, 5.92; S, 47.07. Found: C, 35.12; H, 5.90; S, 46.95.

Dichloroacetaldehyde (6): MS, m/e (relative intensity) 116, 114, 112 (1, 12, 18, M^+) 88, 86, 84 [4, 27, 42, $(M - CO)^+$], 51, 49 [30, 100, $(M - COCl)^+$], 29 (63, CHO^+); t_R = 4.7 min. Authentic sample prepared according to ref.[7]

Methyl bis(methylthio)thioacetate (7): GC/MS, m/e (relative intensity) 182, (5, M^+), 107 [100, $(CH_3S)_2CH^+$]; t_R = 30.6 min.

Synthesis of 7. A mixture of 5.6 g (50 mmol) of **1** and 8.0 g (85 mmol) of dimethyl disulfide was heated to 170 °C in an autoclave for 45 min. The reaction mixture was concentrated in a rotary evaporator at room temperature and 20 torr. The liquid residue was separated by column chromatography (column 2 × 60 cm; 75 g of silica gel; 500 mL of n-pentane and diethyl ether in a volumetric ratio of 95:5) to give 1.5 g of **7** with a purity of 65%. By PGC separation (glass column, 0.8 × 400 cm, 5% Nitrilesilicone oil on Chromosorb G; 60–180 °C at 5 °C/min) of this impure product, a sample of **7** has been isolated: ^1H NMR ($CDCl_3$, Me_4Si) δ 2.19 (s, 6 H), 2.37 (s, 3 H), 4.45 (s, 1 H); IR (film) 1670 cm^{-1} (C=O); MS, m/e (relative intensity) 184, 182 (2, 14, M^+), 156, 154 [1, 7, $(M - CO)^+$], 109, 107 [10, 100, $(CH_3S)_2CH^+$]; t_R = 30.6 min.

Thermal Decomposition of 4a. A small glass tube containing 20 mg of **4a** has been cooled in liquid air, evacuated at 2 torr, sealed, and subsequently transferred to a heating bath at 170 °C for ca. 1 min. The tube was again cooled in liquid air and opened, and the product was admixed with dichloromethane. GLC analysis showed the presence of **4a** (68%), **4b** (5%), **4c** (2%), **4d** (8%), **7** (7%), dimethyl disulfide (2%), and two unidentified components (together 8%).

Attempted Reaction of Dichloroacetaldehyde (6) with Dimethyl Sulfide. A mixture of 0.56 g (4.9 mmol) of **6** and 1.0 g (16.1 mmol) of dimethyl sulfide was kept stirring at room temperature for 48 h. There was no precipitate formed and GLC and ^1H NMR analyses showed the presence of the unreacted starting materials.

Acknowledgment. P. M. Scaria thanks the Alexander von Humboldt-Stiftung (Bonn) for a fellowship.

Registry No. 1, 16650-12-7; **2a**, 101010-52-0; **2b**, 101010-53-1; **3b**, 101010-54-2; **3c**, 101010-55-3; **4a**, 101010-56-4; **4b**, 23328-62-3; **4c**, 101010-58-6; **4d**, 101010-59-7; **5**, 101010-57-5; **6**, 79-02-7; **7**, 101010-60-0; dimethyl sulfide, 75-18-3; ketene, 463-51-4; chloromethane, 74-87-3; sodium methanethiolate, 5188-07-8.

Unusual Temperature-Dependent Isotope Effects in the Reactions of Phenylcarbene with Cyclohexene and Cyclohexane

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The photochemistry of phenyldiazomethane in cyclohexene (cyclohexene-d_{10}) and cyclohexane (cyclohexane-d_{12}) was studied. The chemistry observed was found to be entirely consistent with singlet rather than triplet phenylcarbene reactions. Small (1.9–2.1) isotope effects to CH insertion were observed at 25 °C that increased on cooling. Cooling to very low temperature (−196 °C) reduced the isotope effect. The results are discussed in terms of the hardness of the polycrystalline solid matrix.

Phenylcarbene is the prototypical aromatic carbene and as such has received considerable examination. The triplet has been shown to be the ground state of the carbene by low-temperature EPR.[2] The EPR assignment is quite

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Table I. The Relative Product Yields Obtained on Photolysis of Phenyldiazomethane in Cyclohexene[a]

temp, °C	solv	phase	2	3[b]	syn/anti[d]	k_H/k_D[c]
25	C_6H_{10}	liquid	26	74	1.0	
0	C_6H_{10}	liquid	25	75	1.1	
-30	C_6H_{10}	liquid	25	75	1.2	
-50	C_6H_{10}	liquid	25	75	1.2	
-100	C_6H_{10}	liquid	25	75	1.1	
-135	C_6H_{10}	solid	27	73	1.3	
-196	C_6H_{10}	solid	72	28	1.7	
25	C_6D_{10}	liquid	14	86	0.9	2.2
-100	C_6D_{10}	liquid	10	90	1.0	3.3
-135	C_6D_{10}	solid	24	76	1.1	4.2
-196	C_6D_{10}	solid	47	53		2.9

[a] Absolute yields were not determined; photolysis was carried out with 300-nm Rayonet lamps. [b] Total yields of both syn and anti isomers determined by analytical GC. [c] Calculated by assuming no secondary isotope effect (see text). [d] Errors are ±5%.

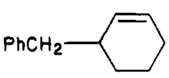
secure as three different carbene precursors can be used to generate the same triplet spectrum. Becker et al. have reported the emission spectrum of matrix isolated phenylcarbene.[3]

Although the triplet is the ground state of phenylcarbene the chemistry of this species in olefin containing solutions is dominated by the low lying singlet state. Photolysis of phenyldiazomethane,[4,5] stilbene oxide[5] or 1,2,3-triphenylcyclopropane[6] generates phenylcarbene, the chemistry of which is largely independent of precursor. The reaction of phenylcarbene with olefins gives cyclopropanes with greater than 95% stereospecificity in all cases, as well as a small (2–5%) amount of allylic CH insertion products. These results have been interpreted to mean that singlet–triplet equilibration in phenylcarbene is more rapid than reaction with olefins.[7] In this view the small equilibrium population of singlet carbene must be much more reactive than the more prevalent triplet state. Support for this interpretation can be found in the work of Baer and Gutsche[8] and of Moss and Dolling.[9] The former group demonstrated that direct and sensitized photolysis of 2-*n*-butylphenyldiazomethane gives the same product distribution which is consistent with rapid spin state equilibration relative to product formation. The latter group demonstrated that the stereospecificity of the addition of phenylcarbene to *cis*-2-butene was not effected by dilution with perfluorocyclobutene as required by a rapid equilibrium mechanism. Recent laser flash photolysis work with diphenylcarbene[10] and fluorenylidene[11] has shown that low lying singlet carbenes can be several orders of magnitude more reactive than their corresponding ground-state triplets and that singlet to triplet carbene intersystem crossing occurs on a subnanosecond time scale.

In 1971 Moss and Dolling discovered that the chemistry of phenylcarbene and *cis*-2-butene depends dramatically on the phase of the reaction mixture.[9] The product mixture is rather invariant with temperature in solution between 0 and −130 °C but changes dramatically in polycrystalline olefin at −160 and −196 °C. Matrix conditions dramatically decrease the yield of cyclopropane products and exalt the yields of olefins. Subsequent to the Moss and Dolling report Moss,[12] Tomioka,[13] and Platz[14] have discovered several more examples of low-temperature matrix effects on carbene reactions. To further elucidate the nature of matrix effects on carbene reactions we have investigated solution and matrix isotope effects on a carbene reaction with an olefinic substrate.

Results and Discussion

We chose to examine the phenylcarbene cyclohexene, cyclohexene-d_{10} system. Cyclohexene was used due to the commercial availability of the deuterated modification, phenylcarbene to maintain contact with the seminal work of Moss and Dolling.[9] A further advantage of this system is that the anticipated reaction products have been described in the literature. These are compound **2**, the product of formal allylic insertion of phenylcarbene **1** and cyclohexene,[15] and the epimeric cyclopropanes **3**. Earlier workers have noted that reaction of phenyl carbenoid with cyclohexene gives predominantly *syn*-**3**. The reported syn/anti ratios are in the range of 2–10 depending on the reaction conditions.[16] In our hands reaction of benzal bromide, cyclohexene, and *n*-butyllithium gives a 6:1 mixture of epimeric cyclopropanes **3**. Accordingly the major isomer is assigned as syn. This material was isolated and characterized.



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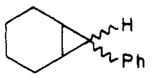

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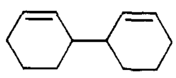
Photolysis of phenyldiazomethane in neat cyclohexene at 25 °C gives a mixture of cyclopropanes **3** and CH insertion adduct **2** with only trace amounts of other compounds. Notable by their absence in the mixture were the radical dimers 1,2-diphenylethane (**4**) and bicyclohexenyl **5** which would be expected from hydrogen abstraction

$\mathrm{PhCH_2CH_2Ph}$ +

4



5

reactions of the triplet carbene. This means that the reaction of phenylcarbene with cyclohexene at 25 °C is predominantly if not exclusively through the low lying singlet state. This view is consistent with that of previous workers.[4-7,9]

The relative yields of **2** and **3** are given in Table I. As expected the cyclopropanes predominate although more CH insertion product is observed than with the simple butenes as a carbene trap. The reaction mixture remains rather invariant upon cooling the solution to −100 °C. This was expected based on the work of Moss and Dolling with *cis*-2-butene[9] and the work of Baer and Gutsche.[8] This means that the two pathways for reaction of singlet phenylcarbene with cyclohexene differ in their entropy of activation with $\Delta S^{\ddagger}$ (cyclopropanation) > $\Delta S^{\ddagger}$ (insertion) but have the same $\Delta H^{\ddagger}$. This has been noted previously by Skell with singlet halocarbenes and olefins.[17] It is even possible that $\Delta H^{\ddagger} \simeq 0$ for singlet phenylcarbene and cyclohexene in light of recent calculations[18] and laser flash photolysis experiments.[19] The syn/anti ratio observed with **3** changes slightly with temperature. The variation is comparable to the experimental error and may not be significant.

We then studied the photolysis of phenyldiazomethane in polycrystalline cyclohexene (the mp of pure cyclohexene is −103.5).[20] At −135 °C **3** is the major product and the ratio of **2**/**3** is similar to that found in solution. However, at −196 °C the ratio of CH insertion product to cyclopropanes increases sharply as expected from the work of Moss and Dolling. The photochemistry of phenyldiazomethane was also studied in cyclohexene-d_{10}, the isotope effect was calculated by taking the ratio of ratios in eq 1

$$(\mathbf{2}/\mathbf{3})_{\mathrm{C_6H_{10}}}/(\mathbf{2}/\mathbf{3})_{\mathrm{C_6D_{10}}} \qquad (1)$$

and assuming that the secondary isotope effect for the cyclopropanation reaction giving **3** was unity. In the cyclohexene-d_{10} polycrystal the cyclopropane products again predominate over the allylic insertion product, as in solutions of cyclohexene. Control experiments with insertion product **2** and syn cyclopropane **3** demonstrated that they are both stable to prolonged photolysis (3000-Å Rayonet) at 77 K.

A small isotope effect of 2.2 was obtained at 25 °C. This is consistent with a singlet insertion reaction which necessarily proceeds by way of a nonlinear transition state.[21] This is in good agreement with the work of Baer, who reported an isotope effect of 2.1 for the reaction of phenylcarbene with cyclohexane.[8] An isotope effect of 2 for the insertion of singlet methylene into the primary CH bond of propane has been reported.[22] The corresponding isotope effect for the reaction of triplet methylene with propane by hydrogen abstraction proceeds by a linear transition state[23] and has a higher isotope effect of 3.1.[22] The reaction of triplet diphenylcarbene with toluene at 25 °C has an isotope effect of 7.0 at 25 °C.[24]

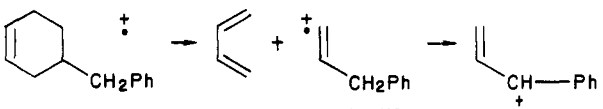
Table II. Intensity of Ions Relative to the Base Peak of Benzylcyclohexenes[a]

	m/e			
	91	92	117	118
2 (3-benzylcyclohexene)	37	5	1	0.1
6 (4-benzylcyclohexene)	53	56	15	6
25 °C photolysis product	43	7	2	1
−196 °C photolysis product	42	8	2	0.4

[a] The base peak of 3- and 4-benzylcyclohexene is *m/e* 81.

The isotope effect for phenylcarbene–cyclohexene in solution at −100 °C is 3.3, 50% larger than at 25 °C. At −135 °C in a polycrystal the isotope effect increases further to 4.2. These three data points correspond to $E_a(\mathrm{D}) - E_a(\mathrm{H}) = 67$ cal/mol and $A_{\mathrm{H}}/A_{\mathrm{D}} = 1.01$. However the isotope effect at −196 °C does not increase to 6.8 as expected from a simple extrapolation of this data but actually decreases to 2.9. This cannot be due to a change of mechanism to triplet carbene chemistry because the triplet is expected to have a larger isotope effect than the singlet carbene. The change in the isotope effect occurs at the same temperature as the change in the product distribution.

One can imagine that phenylcarbene could react with the wrong CH bond in frozen cyclohexene to give 4-benzylcyclohexene (**6**) in addition to **3** and **2**. This can occur in a site in the matrix in which the carbene carbon of **1** is rigidly fixed in a proximal relationship with a homo allylic CH bond. To test this possibility compound **6** was independently synthesized. Unfortunately compounds **2** and **6** could not be separated by capillary GC. Fortunately the mass spectra of **2** and **6** are quite different (Table II). The base peak of each isomer is *m/e* 81 with a large fragment at *m/e* 91 but compound **6** has an intense fragment at *m/e* 92 which is quite weak in the MS of **2**. Furthermore compound **6** undergoes a retro-Diels–Alder fragmentation to give ions unique to this isomer. Reasonably intense fragments at *m/e* 117 and 118 are observed from **6** that are almost entirely absent in the MS of **2**. The GC–MS of benzylcyclohexenes formed on photolysis of phenyldiazomethane in cyclohexene at 25 and −196 °C are virtually the same as pure **3** (Table IV) and indicate that the photolysis mixture does not contain the homoallylic insertion product **6**. This means that phenylcarbene is sufficiently mobile at −196 °C to distinguish between the allylic and homoallylic CH bonds of cyclohexene or that there are no matrix sites in which **1** is rigidly held near a homoallylic CH bond.



6 *m/e* = 118 *m/e* = 117

To test whether the unusual temperature dependence of the isotope effects observed in cyclohexene-d_{10} was unique to this system, the solution and matrix chemistry of phenylcarbene and cyclohexane was examined. Gutsche,

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Table III. The Absolute Yields of Products Obtained by Photolysis of Phenyldiazomethane in Cyclohexane[a,b]

		yield, %			
temp, °C	phase	6	7	stilbene	total
26	liquid	37	3.2	1.9	42
5	liquid	43	4.6	2.1	50
−3	solid	43	6.2	2.7	52
−50	solid	24	14	11	49
−95	solid	1.4	4.5	6.2	12
−145	solid	3.0	4.8	7.6	15
−196	solid	9.2	10	12	31

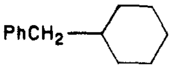
[a] All photolysis were performed in 1:1 cyclohexane/cyclohexane-d_{12} with 7×10^{-2} M phenyldiazomethane. [b] Yields are by GC using naphthalene as an internal standard.

Table IV. Isotope Effects on the Reaction of Phenyldiazomethane with Cyclohexane[a]

temp, °C	M_{174}[f,g]	M_{175}	M_{185}	M_{186}	k_H/k_D
26[b]	21.25	3.03	0.62	11.00	1.9
5[b]	21.38	2.78	0.36	10.13	2.1
−3[b]	21.47	2.98	0.48	10.00	2.1
−50[b]	20.57	1.24	*e*	4.83	4.3
−95[b]	19.85	1.07	*e*	7.27	2.7
−145[b]	22.37	3.08	0.34	8.09	2.8
−196[b]	22.02	2.10	*e*	7.54	2.9
25[c]	31.07	4.49	*e*	*e*	
−196[d]	*e*	*e*	0.72	21.88	

[a] 3.3×10^{-2} M phenyldiazomethane. [b] 1:1 cyclohexane/cyclohexane-d_{12}. [c] Pure cyclohexane. [d] Pure cyclohexane-d_{12}. [e] Intensity of *m/e* too small to measure. [f] The intensity of *m/e* 174 relative to the base peaks. [g] The mass spectra were obtained by GC–MS of benzylcyclohexane formed in the reaction mixture.

Bachman, and Coffy have reported that photolysis of phenyl diazomethane in cyclohexane gives a mixture which is 78% benzylcyclohexane (7) and 22% *cis*-stilbene.[15] We confirm their result (Table III), but in addition we find a small amount of azine 8. We also analyzed for 1,2-diphenylethane (4), benzaldehyde, and bicyclohexyl 9, but these compounds were not detected. All of the components of the mixture were readily separable. The identity of the GC peaks were confirmed by coinjection with authentic samples and by GC–MS. Authentic benzylcyclohexane was synthesized by reduction of phenyl cyclohexyl ketone with trifluoracetic acid and triethylsilane.



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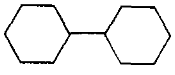
PhCH=NN=CHPh

8



9

Photolysis of phenyldiazomethane in cyclohexane (Rayonet 3000 Å) gave the product mixtures shown in Table III. The yields are not corrected for unreacted phenyldiazomethane, which was consumed by the addition of acrylonitrile. The low material balances reflects the difficulty of purifying and weighing small amounts of phenyldiazomethane. The still lower material balance observed in solid cyclohexane is a consequence of incomplete photolysis of the diazo precursor in the matrix. The only significant products observed in solution or in the matrix were benzylcyclohexene (7), stilbene, and azines. The complete lack of radical dimers 4 and 9 in the solution phase product mixtures suggests that in this phase 7 is formed entirely by an insertion reaction of singlet phenylcarbene rather than by a radical–radical coupling process derived from the triplet. This view is confirmed by analysis of the benzylcyclohexanes formed in a 1:1 solvent mixture of cyclohexane–cyclohexane-d_{12}. The isotope effect of 1.9 at 26 °C was determined by the ratio of M_{174}/M_{186} and is very close to the value reported by Baer and Gutsche[8] and similar to that in the phenylcarbene–cyclohexene system. Significantly, no cross-coupling products such as 10 or 11 were observed thus ruling out a triplet origin of the benzylcyclohexanes (see Table IV).

$PhCHDC_6H_{11}$ **10**

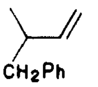
$PhCH_2C_6D_{11}$ **11**

The isotope effects measured within an 8 °C range at 5 (solution) and −3 °C (matrix, the mp of pure cyclohexane is 6.5 °C)[20] are both the same and only slightly higher than that at 26 °C. This demonstrates that a change of phase alone is not enough to affect the size of the isotope effect. At −50 °C the isotope effect increases to 4.3, but further cooling to between −94 and −196 °C leads to reduced isotope effects of 2.7–2.9. The phenylcarbene–cyclohexane system exhibits the same qualitative temperature-dependent isotope effects as does phenylcarbene–cyclohexene. It is not surprising (vide infra) that the break in the isotope effects observed in cyclohexane occurs at a much higher temperature than cyclohexene when one considers the difference in melting points of these substances.

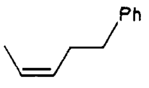
We believe that these results are a consequence of the changing "hardness" of the polycrystalline matrix as a function of temperature. The hardness of a polycrystal is a nebulous concept as difficult to define as to measure. The range of motion available to phenylcarbene in a "hard" matrix must be quite restricted. In a "soft" matrix phenylcarbene will be more mobile and can display some chemical selectivity. In this view cyclohexane at −3 and −50 °C must be relatively soft as normal isotope effects are observed. Phenylcarbene must be mobile enough in solid cyclohexane between −3 and −50 °C to distinguish CH and CD bonds as in solution. Solid cyclohexane is hard between −95 and −196 °C. The larger than expected amounts of formal CD insertion products formed in cyclohexane between −95 and −196 °C are due to sites in the matrix in which a rigid phenylcarbene can only react with a carbon–deuterium bond. The matrix lowers the isotope effects by preventing a free competition.

The data for the phenylcarbene–cyclohexene system can be interpreted in a similar fashion. Phenylcarbene must be relatively mobile in solid cyclohexene at −135 °C and the choice of reaction with a carbon–carbon double bond or a carbon–hydrogen (deuterium) single bond is influenced by temperature as well as by phase. Cyclohexene must be rather hard at −196 °C, and the preferred reaction pathway is determined more by whether a CD or a CH bond is near the rigidly held carbene than by the mass of hydrogen or deuterium. Interestingly, phenylcarbene is sufficiently mobile in cyclohexene at −196 °C to distinguish between allylic and homoallylic CH bonds.

Moss and Dolling have interpreted the increased yields of olefins 12 and 13 in the reaction of phenylcarbene with solid *cis*-2-butene[9] as a consequence of increased triplet reaction in the matrix. Rearranged olefin 12 must surely arise from the benzyl–butenyl radical pair 14. Olefin 13 can be formed from 14 as well, but it can also be formed by an insertion reaction of the carbene. Further evidence of triplet phenylcarbene chemistry in solid isobutene was provided by C-13 labeling experiments.[12]



12



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14

In light of Moss's work it would seem likely that the increased yields of 2 in solid cyclohexene have a triplet origin. This would make the isotope effects measured in the polycrystals still lower than expected. It must be noted, however, that our data, by itself, is equally consistent with a pure singlet carbene reaction. In this view the matrix retards cyclopropanation relative to insertion. We have no spectroscopic data to support triplet involvement in the phenylcarbene–cyclohexene system as photolysis of phenyldiazomethane in cyclohexene or cyclohexene-d_{10} at −196 or −269 °C does not produce detectable triplet carbene EPR spectra. This means that triplet phenylcarbene is not formed in frozen cyclohexene or its lifetime is extremely short ($t_{1/2} < 1$ min).

Experimental Section

Cyclohexane-d_{12} and cyclohexene-d_{10} were purchased from Merck, Sharpe and Dohme. Photolyses were performed with two Southern New England Ultraviolet Rayonet Reactor lamps RPR 3000 using a Pyrex filter. These lamps have maximum emission at 300 ± 30 nm. The use of Pyrex tubes means that the samples were irradiated principally between 310 and 330 nm. The temperature was controlled by blowing nitrogen gas through a coil immersed in liquid nitrogen. The temperature was monitored with an Omega digital thermometer. Samples were degassed by three freeze–pump–thaw cycles and sealed in Pyrex tubes which had been washed with ammonium hydroxide. Samples were photolyzed until the red color of phenyldiazomethane was completely bleached. This required 2 h for solution-phase samples and 5–7 h for solid-state samples. For the low-temperature solids glass rods were inserted into the tubes to maximize the surface area of the sample and increase the efficiency of the photolysis. The samples were stored in liquid nitrogen until analyzed on a Hewlett-Packard 5830 GC with a 6-ft 10% SE-30 column. Acrylonitrile was added to the samples prior to GC analysis to consume unreacted phenyldiazomethane. Samples were analyzed by GCMS at the Campus Chemical Instrumentation Center using a Finnegan 4125 GG MS data system.

3-Benzylcyclohexene (2).[15] In a 25-mL three-neck round-bottom flask equipped with an addition funnel, reflux condenser, nitrogen inlet, and magnetic stirrer bar was placed 290 mg (12.1 mmol) of magnesium turnings and 5.0 mL of dry ether. A solution of 0.34 mL (2.38 mmol, 1.0 equiv) of benzyl bromide in 3.0 mL of ether was then slowly added dropwise until the reaction began. The rest of the solution was added at a rate sufficient to maintain the reaction. The solution was stirred for 2 h at room temperature, then the supernatant containing the Grignard reagent was transferred to another 25-mL round-bottom flask equipped with an addition funnel and a magnetic stirrer bar. A solution of 0.25 mL (2.38 mmol, 1.0 equiv) of 3-bromocyclohexene in 5.0 mL of ether was then slowly added in dropwise over 10 min. The solution was stirred at room temperature for 17 h, and a white precipitate developed. The reaction was quenched with 10 mL of saturated NH_4Cl solution. The layers were separated, and the aqueous layer was extracted with 10 mL of ether. The combined ether layers were dried over Na_2SO_4 and concentrated in vacuo to give 356 mg of an oil. The crude reaction product was chromatographed on a 14.0 × 2.0 cm silica gel column by using flash chromatography. Elution proceeded as follows with hexane as the eluant: 40 mL, nil; 60 mL, 225 mg of a colorless oil. GC analysis (6 ft × $^1/_8$ in. 10% SE-30 column) indicated the oil contained 97% pure **2**. The material was chromatographed on another 14.0 × 2.0 flash silica gel column and eluted with hexane as follows: 60 mL, a small amount of an unidentified impurity; 50 mL, 146 mg of **2** as a colorless liquid: NMR (200 MHz, $CDCl_3$) δ 7.32–7.15 (m, 5 H), 5.67–5.53 (m, 2 H), 2.66–2.35 (m, 3 H), 2.02–1.24 (m, 5 H); IR (CCl_4) 3025 (m), 2930 (s), 2855 (m), 1493 (w), 1455 (m), 692 (m), 668 (m); exact mass obsd 172.126, calc 172.125.

***syn*-2-Phenyl[4.1.0]bicycloheptane (3).**[6] In a 25-mL round-bottom flask equipped with an addition funnel and magnetic stirrer bar was placed 10 mL of cyclohexene. The flask was cooled to −20 °C in an ethylene glycol/CO_2 slush bath, and then 0.50 mL (0.0030 mol, 1.0 equiv) of benzal bromide was added. The solution was stirred, and 2.25 mL (1.2 equiv) of a 1.6 M solution of *n*-BuLi (Aldrich) in pentane was added dropwise over 15 min. The cloudy white solution was stirred at −20 °C for 15 min and then at room temperature for 3 h. The reaction mixture was washed with 2 × 10 mL of water, dried over Na_2SO_4, and concentrated in vacuo to give 677 mg of an orange liquid. TLC (100% hexane, silica gel) indicated the presence of four components. The crude mixture was purified by flash chromatography using a 4.0 × 2.0 cm silica gel column and elution with hexane as follows: 50 mL, nil; 10 mL, 61 mg of syn cyclopropane **3** as a colorless liquid: NMR (200 MHz, $CDCl_3$) δ 7.31–7.08 (m, 5 H), 2.00–1.60 (m, 3 H), 1.31–0.64 (m, 8 H); IR (CCl_4) 2930 (s), 2860 (m), 1450 (m), 695 (m); exact mass obsd 172.126, calc 172.125.

Benzylcyclohexane (7).[26] In a 15-mL round-bottom flask equipped with a nitrogen inlet and magnetic stirrer bar were placed 400 mg (2.13 mmol) of phenyl cyclohexyl ketone (Aldrich) and 7.0 mL of freshly distilled trifluoroacetic acid. Triethylsilane (1.4 mL, 4 equiv) was then added dropwise with vigorous stirring. The solution was stirred for 18 h at room temperature, and then 20 mL of saturated $NaHCO_3$ solution was added. The mixture was extracted with 2 × 10 mL of ether. The ethereal solution was washed with 5 × 10 mL of saturated $NaHCO_3$ solution, dried over Na_2SO_4, and concentrated in vacuo to afford 290 mg of a colorless liquid. The crude reaction product was purified by flash chromatography using a 9.0 × 2.0 cm silica gel column. Elution proceeded as follows: 100% hexane, 20 mL, nil; 40 mL, 265 mg of **6** as a colorless liquid: NMR (200 MHz, $CDCl_3$) δ 7.26–6.90 (m, 5 H), 2.43 (d, $J = 6$ Hz, 2 H), 1.83–0.74 (m, 11 H); IR (CCl_4) 2920 (s), 2850 (m), 1450 (m) cm^{-1}; exact mass obsd, 174.141, calcd 174.142.

Phenyldiazomethane (1) was prepared by the method of Farnum[25] and purified by trap-to-trap distillation [room temperature to −80 °C (1 mm)] and used immediately.

4-Benzylcyclohexene (5) was prepared by the method of Ceder and Nilsson.[27]

Acknowledgment. We are indebted to the National Science Foundation for support of this work. GC–MS were produced at the Ohio State Campus Chemical Instrumentation Center.

Registry No. **2**, 4714-10-7; **3**, 10503-36-3; **7**, 4410-75-7; phenylcarbene, 3101-08-4; deuterium, 7782-39-0; phenyldiazomethane, 766-91-6; cyclohexane, 110-82-7; benzyl bromide, 100-39-0; 3-bromocyclohexene, 1521-51-3; benzal bromide, 618-31-5; phenyl cyclohexyl ketone, 712-50-5.

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