Tetrahedron Vol 41, No. 8, pp. 1517 to 1523, 1985
Printed in Great Britain.

0040-4020/85 \$3.00 + .00
Pergamon Press Ltd.

THE CHEMISTRY OF CARBENES IN LOW TEMPERATURE RIGID MEDIA

BRADFORD B. WRIGHT†
Department of Chemistry, Yale University, New Haven, CT 06511, U.S.A.

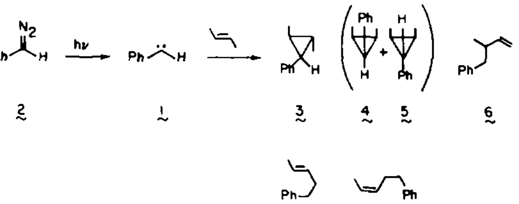
(*Received in USA* 10 *December* 1983)

Abstract—The use of frozen organic matrices to study the chemistry of arylcarbenes is discussed. Also the effects of the matrix environment on bimolecular reactions are explored.

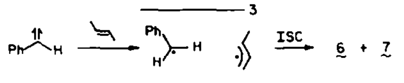
The reactivity of divalent C has been an active field of study since Hine[1] demonstrated the intermediacy of dichlorocarbene in 1950. Subsequently, the chemistry of these highly reactive intermediates in liquid solution has been extensively investigated.[2] Over the past twelve years reports have also appeared in the literature concerning the reactions of carbenes in frozen organic matrices. This has proven to be a rich field of chemistry providing both information on carbene reactivity and on matrix influences on bimolecular reactions. The following discussion attempts to provide an overview of these experimental findings and their implications in the area of solid state carbene chemistry.

Alkene matrices

In 1971 Moss and Dolling[3] investigated the chemistry of phenylcarbene (**1**), in 2-butenes over the temperature interval 0 to −196°. These workers monitored the relative yields of products **3–8** resulting from the photolysis of phenyldiazomethane (**2**). At 0° in neat *trans*-2-butene the major product found was **3** (94%), resulting from stereospecific cyclopropanation. Small amounts of the olefinic products **6** and **7** were also observed (2 and 4%, respectively).



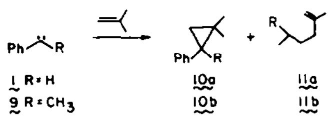
In contrast, at −196° under matrix conditions a reduced yield of **3** (70%), was found with a corresponding increase in **6** (16%) and **7** (7%). When *cis*-2-butene was used as solvent striking results were obtained. In this case **8**, present in trace amounts in liquid solution from 0 to −70°, became the major product at −196° (50% yield relative to isolated material). Products **6–8** were proposed to result from a H atom abstraction–recombination (*a–r*) mechanism involving 2-butene and triplet phenylcarbene (**1T**). This assumption was based on earlier work of Gibbons and Trozzolo[4] who found by ultraviolet spectroscopy that diphenylmethyl radical is formed in the decay of diphenylcarbene in organic glasses at low temperature, and on the known ability of triplet methylene as well as other carbenes to abstract hydrogen atoms in the gas and liquid phases.[5] The possible intervention of C—H bond insertion via the singlet state of phenylcarbene (**1S**) was not discussed.



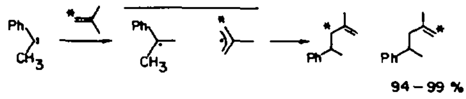
Within the framework of the above model these results indicated that the matrix environment can enhance triplet chemistry. The cause of this effect was explained in terms of a rapid thermally driven singlet–triplet (S–T) equilibrium in which competing processes occur from both states. In this model (see Fig. 1), the matrix acts to slow k_2 relative to k_3 leading to an increase in production of **6** and **7** over **3**.

Liquid phase reactions of **1** in 2-butene were shown to give products of radical–radical cross coupling (e.g. bibenzyl), yet these products were not found among the reaction products under matrix conditions. Therefore, it should be noted that if **6–8** arise via an *a–r* mechanism, then the matrix environment must impose restrictions on the chemistry of the resultant radical pairs.

The suggestion that the matrix environment can enhance triplet carbene chemistry was further supported in 1977 when Moss and Joyce[6] examined the chemistry of **1** and phenylmethylcarbene (**9**), in isobutene solutions ranging from 0 to −120°. In both cases continued cooling resulted in the formation of alkenes **11a**, **11b** (the products of formal allylic insertion). At −196° the ratios **11a**/**10a** and **11b**/**10b** were 1.3 and 2.8, respectively.



The mechanism responsible for the formation of **11b** was investigated by the following ^{13}C labelling experiment:



---

† Present address: Science Research Laboratory, 3M Company, St. Paul, MN 55144, U.S.A.

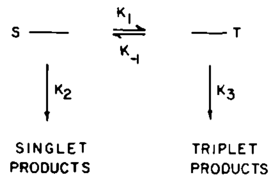
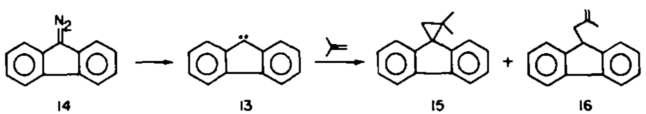


Fig. 1. Kinetic scheme for S–T equilibration leading to product formation.

At −196° **9** gave about 6% of the "rearranged" product. Further studies by Moss and co-workers[8,9] with diphenylcarbene (**12**), and fluorenylidene (**13**), under the same conditions led to 28% and 50% "rearranged" product, respectively. These results have been rationalized by an *a–r* mechanism in which the extent of rearrangement is directly proportional to the lifetime of the intermediate radical pair. Thus, the highly stabilized fluorenyl radical shows the most rearrangement while the least stabilized benzyl radical collapses most rapidly with inefficient scrambling of the label.

Moss and Joyce[8] also examined the chemistry of **13** at low temperatures. Again in isobutene solution, photolysis of diazofluorene (**14**) gave a >94% yield of cyclopropane **15** with only 4% of the formal C—H insertion product **16**. As before, at −196° in the solid state the yield of **15** fell drastically to 58% while that of **16** increased to 39%. At this point, these workers proposed that the observed changes in chemistry on going from liquid to solid phase could be entirely explained in terms of a simple temperature dependent equilibrium such as that shown in Fig. 1. For a carbene S–T equilibrium in which the triplet prevails as the ground state, lower temperatures result in an increase in the fraction of carbenes present in the triplet form. Thus, an increase in **13T** leads to an increase in the yield of **16**.

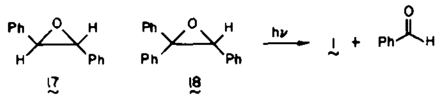


14 **13** **15** **16**

Moss and Huselton[9] have extended this argument to the reaction of **12** in isobutene and observed a linear temperature dependence for the ratio ln (cyclopropane/alkene) with 1/T over the temperature range 0 to −196°. Such a temperature dependence is predicted for a kinetic scheme in which **12S** is in rapid equilibrium with **12T**. In this case, **12S** would lead to cyclopropane formation while **12T** would lead to alkenes. The success of a temperature dependent equilibrium model to account for the observed chemistry in both liquid and solid phase is remarkable. Typical viscosities in hydrocarbon matrices range from 10^4 to 10^{12} poise while liquid phase values run from 10^{-2} to 10^{-3} poise.[10] Thus, one might expect substantial differences in chemistry on changing the reaction phase.

Matrix effects

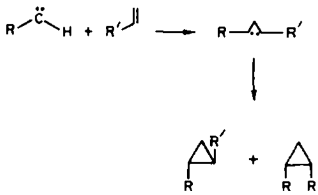
Such behavior has been observed by Tomioka *et al.*[11] These workers demonstrated that the product distribution in solid state carbene reactions varies with precursor. Compounds **2**, **17**, and **18**, all photochemical precursors of **1**,[12] gave identical product distributions when photolyzed in 2-propanol solutions. On the other hand, the product distributions in 2-propanol matrices showed a marked variation with precursor structure. Their results indicate that depending on the geometry of the precursor, the nascent carbenes are generated with different spatial relationships to the host molecules of the matrix. The product distribution is then determined by the nature of the particular matrix sites in which the carbenes are formed.



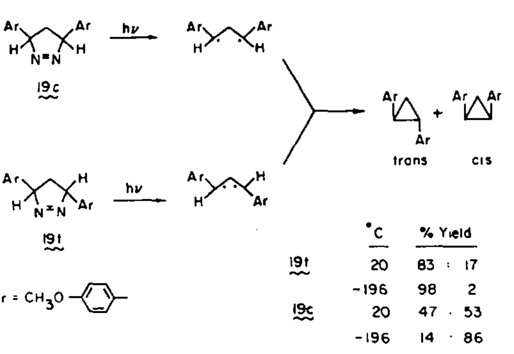
17 **18** **1**

Under the rigid conditions of the matrix environment reactions take place with a minimum of molecular motion. Schmidt[13] has coined the term "Topochemical Principle' to refer to this effect. According to this principle relative yields in solid state reactions are often determined by transition state perturbations or by the relative rates of diffusion processes which establish a suitable geometry for reaction.[14] Such processes may be rotational or translational. It is possible that in Moss and Huselton's study of **12** that the motion of individual solvent molecules within the matrix environment is still sufficiently large to allow the nascent carbene a choice of reactive pathways. If this is the case, then one might expect carbene intermolecular reactions to exhibit strongly phase dependent behavior in addition to any temperature effects.

Tomoika *et al.*[15] have examined the effects of reaction phase on the stereoselectivity of 1,3-diradical ring closure. Such diradicals are presumably involved in the addition of triplet carbenes to alkenes resulting in cyclopropane formation.



Photolysis of azoalkanes **19c**, **t** as illustrated in Fig. 2 leads to two isomeric 1,3-diradicals (*cis* and *trans*),

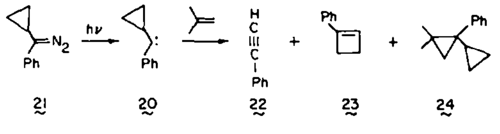


	°C	% Yield
19t	20	83 : 17
	−196	98 2
19c	20	47 · 53
	−196	14 · 86

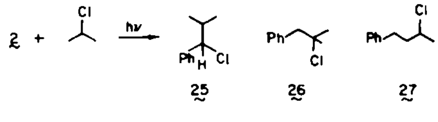
Fig. 2. Matrix influences on diradical closure.[15]

which either close or interconvert. In solution the rate of interconversion is comparable to the rates of ring closure, but in the solid phase the rate of interconversion is dramatically lower. This can be seen in the increased formation of cyclopropanes bearing the same configuration of aryl substituents as the parent azoalkane used in the photolysis. This result provides evidence that rotation of the 1,3-diradical becomes severely hindered in the matrix environment.

In view of this behavior it seems reasonable to expect that carbenic unimolecular rearrangements might also exhibit a strong topochemical influence due to the need for specific transition state geometries. This possibility was explored by Moss and Wetter[16] in a study of the rearrangement processes of phenylcyclopropylcarbene (**20**), in isobutene. Photolysis of **21** in isobutene solution at 25° gave a 16% yield of **22** with 63% of cyclobutene **23**, and 2% of the intermolecular addition product **24**. In liquid solutions a linear dependence of ln (**23**/**24**) *vs* 1/T was established resulting from competitive reactions with different activation energies. However, in the solid state the ratio of **23**/**24** was much lower than predicted by the above analysis. This phenomenon appears to reflect a matrix constraint on the geometry of the transition state geometry of the intramolecular ring expansion. Therefore, any temperature dependent equilibrium model for carbene matrix reactions such as that depicted in Fig. 1 must take into account the potential for matrix steric effects.

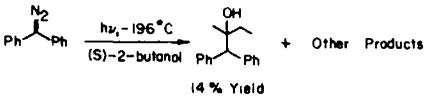


Tomioka *et al.*[17] have investigated the reactions of **1** in 2-chloropropane. In this system two distinct types of matrix effect were observed. In solution insertion of **1** into the C—Cl bond to give **25** occurred readily and increased at the expense of **26** as the reaction temperature was lowered. Compound **27** appears to have been completely absent from liquid phase photolyses.



On transition from the liquid to the solid phase **25** was "completely diminished", and **26** and **27** became the major products, the origin of this matrix effect was not clearly established.[18] A second and quite general matrix effect was seen in the increase of **27** in the solid state (from a trace in solution at 0° to 11% at −196° under matrix conditions). The formation of **27** appears to result from reaction of **1** at sites within the matrix in which the only accessible bonds for reaction with the carbene are those of the solvent Me groups. The weaker secondary C—H bond which is attacked preferentially in solution may therefore be completely inaccessible in many matrix sites.

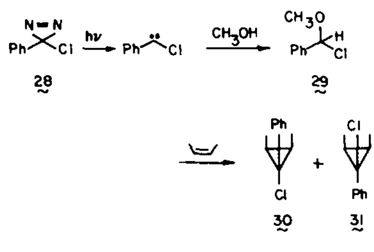
The stereochemistry of formal C—H carbene insertion reactions under matrix conditions has been recently studied by Zayas and Platz.[19] These workers generated **12** in an optically active (*S*)-2-butanol matrix. At −196° they isolated the product of formal C—H insertion at C(2) in 14% yield and demonstrated that it is formed enantiomerically pure. The specific configuration was not determined, but it seems almost certain that retention of configuration at the reacting carbon was observed. Such a result could be accounted for by either a direct insertion mechanism or an *a–r* mechanism with a matrix memory effect on radical recombination. Their results do indicate though that if reaction occurs by H-atom abstraction that there is insufficient mobility within the matrix to allow for racemization to occur.



Spin state reactivity

The ability of singlet carbenes to insert into the O—H bond of alcohols has been widely established.[20] The possibility that insertion may also occur from the singlet state into the C—H bonds of alcohols is less well understood. Tomioka *et al.*[21] have investigated this question and provided circumstantial evidence against singlet C—H insertion.

These workers irradiated phenylchlorodiazirine (**28**), in methanol at temperatures from 0 to −196°. Over this temperature interval clean formation of the O—H insertion product **29** was observed. Additionally, photolysis of **28** in neat *cis*-2-butene at −196° gave a mixture of cyclopropanes **30** and **31** resulting from stereospecific cycloaddition to the double bond. This contrasts with the behavior of **1** which gave 40% C—H insertion into methanol and 30% allylic C—H insertion into *cis*-2-butene at −196°.



All available evidence indicates that phenylchlorocarbene is a ground state singlet while **1** is a triplet.[22] Thus, it appears that O—H insertion and cyclopropanation are preferred reactions of the singlet state while C—H insertion occurs only from the triplet state. The possibility that O—H insertion may occur from the triplet state of carbenes cannot be ruled out on the basis of the existing experimental data, but the likelihood of such a process seems small when the propensity of triplet carbenes to attack the weakest bond in the molecule and the large O—H bond dissociation energy ($\sim$103 kcal/mol) are taken into account.[23]

Alcohol matrices

Perhaps the most intriguing and potentially informative aspect of carbene matrix chemistry concerns their reactivity in alcoholic matrices. Tomioka and Izawa[24] have extensively studied the chemistry of **1** and **12** in a variety of alcoholic solvents (MeOH, EtOH, 2-PrOH). A summary of their results shown in Table 1 indicates that in every case the yield of ethereal products resulting from O—H insertion decreases substantially on cooling. This decrease is accompanied by an increase in C—H insertion products. If one accepts the notion that singlet and triplet carbenes react with O—H and C—H bonds, respectively, then an increase in triplet chemistry is observed at lower temperatures. These findings are then at least qualitatively consistent with the S–T equilibrium model of Fig. 1.

Close examination of Table 1 also shows a topochemical matrix effect on the formation of primary C—H insertion products. The sharp increase in the formation of these products on transition to the solid state is consistent with other studies of Tomioka[25] on the reactivity of **1** in hydrocarbon solvents and is the same effect noted earlier in the case of 2-chloropropane matrices.

It is interesting that when t-butanol is used as solvent[26] no primary C—H insertion is observed even at −196°. Instead, carbene dimers are formed (possibly on thawing the matrix for analysis). To account for the low reactivity of **1** with t-butanol it has been suggested that the diazo precursor forms microcrystals within the matrix on cooling. The carbenes which subsequently are formed can then only react with other carbenes to give dimers. Within this context, as long as solubility is maintained during the freezing process reactivity with the matrix can be expected.

Platz *et al.*[27] have investigated the effects of matrix isotopic substitution on the reactivity of **12**. In 2-propanol at −196° it was shown that deuterium substitution at C resulted in reduced yields of C—H(D) insertion products (Table 2). It is possible that this observation results from a kinetic scheme such as that of Fig. 1 in which the intersystem crossing of T → S is rate determining followed by rapid O—H insertion. In this scheme the relative yield of O—H insertion products would be dependent on the S–T splitting.

Tomioka *et al.*[28] have suggested that this may be the case in the reactions of **1** with alcoholic matrices. By varying substituents on the phenyl group a change in the ratio of O—H/C—H insertion was effected. At low temperature both electron donating and withdrawing substituents facilitate O—H insertion. The cause of this behavior may involve a change in the mechanism of O—H insertion or a substituent effect on the S–T energy gap.

α-Ketocarbenes

The question of carbene reactivity in matrices has been extended to α-ketocarbenes as well.[29] In contrast to the case of simple aryl carbenes the chemistry of these carbenes is quite complex. Phenylcarbomethoxycarbene (**32**), displays a marked increase in C—H insertion into 2-propanol under matrix conditions (from 4% at −77° to 63% at −196°). On the other hand carbomethoxycarbene (**33**), shows only a slight increase in C—H insertion on going from liquid solution to the solid phase. Also, Wolff rearrangement of **32** was

Table 1. Product distributions in the reactions of arylcarbenes with alcohols at various temperatures[a]

Carbene	Temp. °C	Phase	Alcohol	Relative yield: O—H insertion	Relative yield: C—H insertion at hydroxylic C	Relative yield: C—H insertion at primary C
1	0	L	EtOH	94.9	5.1	—
	−78	L		88.5	11.5	—
	−110	L		80.6	18.1	1.3
	−155	C		45.7	51.2	3.1
	−196	C		23.2	71.5	5.3
12	0	L		100.0	—	—
	−78	L		99.9	0.1	—
	−110	L		97.2	0.2	—
	−155	C		93.5	6.2	0.3
	−196	C		48.3	37.8	13.9
1	0	L	2-PrOH	80.9	18.5	0.6
	−78	L		64.0	34.9	0.1
	−110	C		38.5	49.9	11.6
	−196	C		15.8	68.5	15.7
12	0	L		99.9	0.1	—
	−78	L		99.7	0.3	—
	−110	C		91.2	8.1	0.7
	−196	C		31.8	52.7	15.5

[a] Data adapted from ref. 24.

Table 2. Chemical isotope effects in the reaction of diphenylcarbene with isotopically labelled 2-propanols at $-196°$[a]

Matrix	Ø$_2$CHOCH(CH$_3$)$_2$	Ø$_2$CH$\overset{\text{OH}}{\text{C}}$(CH$_3$)$_2$	Ø$_2$CHCH$_2$$\overset{\text{OH}}{\text{C}}HCH_3$
$CH_3CHOHCH_3$	24.6	54.5	20.9
$CH_3CHODCH_3$	22.8	52.4	24.8
$CD_3CHOHCD_3$	26.4	73.6	trace
$CH_3CDOHCD_3$	45.1	13.6	41.3
$CD_3CDODCD_3$	67.9	32.1	trace

[a] Products normalized to 100%; ref. 27.

almost entirely suppressed under matrix conditions while no effect was seen in the case of **33**. To complicate matters further **33** can apparently give formal C—H insertion directly from the singlet state.

Additionally, possible reactions of the excited singlet state of the diazoketone (e.g. Wolff rearrangement) must be considered. The experimental results were explained in terms of substituent effects on the S–T gap. If the gap in **33** is small, then reaction could occur exclusively via the singlet state while the presence of a phenyl group in **32** could possibly widen the gap and cause reaction to occur from both states in solution while allowing only triplet reactions in the matrix. This argument is supported by related work on the temperature and phase dependence of C—H insertion by a number of aliphatic carbonylcarbenes.[30] The reader is referred to the rather detailed discussion therein for more information on the subject.

In the case of phenylphosphorylcarbene Tomioka *et al.*[31] have shown that the reactivity is analogous to that of simple arylcarbenes in both the liquid and solid phases.


32


33

Matrix kinetics

The reactivity of triplet arylcarbenes in frozen matrices has been investigated by Electron Spin Resonance spectroscopy. A preliminary account using this approach was published in 1980 by Lin and Gaspar[32] who examined the decay of **1**, **12**, and **13** in isobutene and Fluorolube matrices. Subsequently, Platz *et al.*[33] have extensively studied the reactions of triplet arylcarbenes in organic matrices by this method.

In typical experiments utilizing this method a carbene precursor is placed in a quartz tube containing the organic solvent desired. The tube is cooled to the desired temperature and photolyzed briefly in the microwave cavity of an ESR spectrometer. After shuttering the light source kinetics are obtained by monitoring the natural logarithm of the signal intensity with respect to time. In this way pseudo-first order rate constants can be measured for reactions of triplet carbenes with the matrix. Nonlinear kinetic decay is generally seen as the percentage of signal decay becomes larger than 10–20%. This phenomenon has been observed in other matrix reactions and has been termed composite-first order kinetic decay by Willard.[34] The origin of this effect appears to lie in the existence of a distribution of carbene orientations with respect to the host matrix. One solution to the problem has been to examine only the initial portion of the signal decay over which a plot of ln (intensity) *vs* time remains linear. The results presented herein were obtained by this approach.

Senthilnathan and Platz[33a,b] investigated the reactivity of 1-naphthylcarbene, diphenylcarbene, and fluoroenylidene by this method. Some of their results are presented in Table 3. Evidence of a matrix isotope effect indicates that a bimolecular process is being monitored by the ESR method. Among the most intriguing of their findings was the observation of unusually low Arrhenius parameters for the reaction of these carbenes with hydrocarbon matrices. This

Table 3. Rate constants and Arrhenius parameters for carbene reactions in organic matrices[a]

Carbene	Matrix	k_{EXPT}, s^{-1} at 77 K	log A	Ea cal/mol	A_D/A_H
1	toluene	0.00321	1.24	1671	
	toluene-d_8	0.00014	3.36	2878	130
13	toluene	0.0051	0.85	1571	
	toluene-d_8	0.0018	2.14	2008	20
12	ether	0.0022	5.4	2900	
	ether-d_{10}	0.00019	7.4	4000	100
	MCH[b]	—	2.3	2800	
	MCH-d_{14}	—	3.6	3600	20
	toluene	0.00063	2.4	2100	
	toluene-d_8	—	3.6	3100	16

[a] Data from refs 27, 33*a*.
[b] Methylcyclohexane.

Table 4. Tunneling parameters for H-atom abstractions by diphenylcarbene.[a]

Matrix	V_1[b] kcal/mol	a_1[c] Angstroms	Number of points
methylcyclohexane	14.1	1.04	5
methylcyclohexane-d_{14}	13.7	0.694	5
diethyl ether	11.4	1.37	4
diethyl ether-d_{10}	10.4	0.940	4
2-propanol	13.2	1.18	4
toluene	12.9	1.25	5
toluene-d_8	12.8	0.766	5

[a] Data taken from ref. 27.
[b] Eckart barrier height parameter.
[c] Eckart barrier width parameter.

observation prompted these authors to suggest that a quantum mechanical tunneling mechanism might be involved in the low temperature H-atom abstraction reactions of carbenes. This was supported by the ratios of A_D/A_H in Table 3. Bell[35] has stated that values of A_D/A_H in excess of 2 are outside the limits of classical theory and may be considered indicative of tunneling.

The term tunneling as used here refers to the process by which a particle of energy E can traverse a potential barrier of energy $V > E$. This phenomenon is a consequence of the wave-particle duality of matter and is sensitive to the height and especially the width of the potential barrier. Readers wishing further information on the subject are referred to the excellent discussion by Bell.[35] LeRoy *et al.*[36] have developed a one dimensional model employing an Eckart potential barrier for use in calculating tunneling rates. This model has been applied to arylcarbene decay processes by Platz *et al.*[27,33c] Good agreement between observed and calculated rate constants for diphenylcarbene decay in a number of H(D)-atom donating matrices was found (see Table 4). The results obtained were of comparable quality to those of LeRoy *et al.* in their study of H-atom abstraction reactions by methyl radicals. The ability to reconcile theory and experiment provides circumstantial evidence of tunneling.

Typical barrier parameters were heights of 10–15 kcal/mol and widths of 0.7–1.0 Angstroms. Although the widths calculated for the barrier parameters seem plausible it appears likely that the barrier heights may be too high. However, it must be pointed out that the model being used is a crude one dimensional representation of a multidimensional problem, and as such one should not attempt to overinterpret numerical results. In spite of the success of the theoretical model in duplicating the experimental results it remains a clear possibility that the results may be fortuitous due to experimental artifacts. Further experiments are needed to clarify the issue.

CONCLUSION

The matrix chemistry of arylcarbenes can be explained in terms of a thermal S–T equilibrium in which the relative amounts of triplet and singlet chemistry are determined by the S–T energy gap and by the rate constants for reaction from each state. The available evidence suggests that O—H insertion and stereospecific cyclopropanation are the characteristic reactions of the singlet state, while H-atom abstraction and nonstereospecific cyclopropanation are the characteristic reactions of the triplet state. It is clear that the effects of the rigid matrix environment can alter the reactivity of H-atom abstraction processes as evidenced by the formation of primary C—H insertion adducts, yet the magnitude of such effects remains unclear.

The ability to enhance triplet reactivity under low temperature matrix conditions suggests that further study to increase our understanding of this phenomenon will utimately provide a useful diagnostic tool in the study of the reactivity of carbenes in general.

REFERENCES AND NOTES

[1] J. Hine, *J. Am. Chem. Soc.* **72**, 2438 (1950).

[2] For reviews see [a]W. Kirmse, *Carbene Chemistry*. Academic Press, New York (1964); [b]*Carbenes* (Edited by M. Jones Jr. and R. A. Moss), Vol. 1, Wiley, New York (1973); Vol. 2 (1975).

[3] R. A. Moss and U.-H. Dolling, *J. Am. Chem. Soc.* **93**, 954 (1971).

[4] W. A. Gibbons and A. M. Trozzolo, *Ibid.* **88**, 172 (1965).

[5a] Ref. 2; [b]R. W. Carr Jr., *J. Phys. Chem.* **70**, 1971 (1966); [c]B. M. Herzog and R. W. Carr Jr., *Ibid.* **71**, 2688 (1967); [d]M. L. Halberstadt and J. Crump, *J. Photochem.* **1**, 295 (1972).

[6] R. A. Moss and M. A. Joyce, *J. Am. Chem. Soc.* **99**, 1262 (1977); see also R. A. Moss and M. A. Joyce, *Ibid.* **99**, 7399 (1977) (correction).

[7] Refs 6 and 9.

[8] R. A. Moss and M. A. Joyce, *J. Am. Chem. Soc.* **100**, 4475 (1978).

[9] R. A. Moss and J. K. Huselton, *Ibid.* **100**, 1314 (1978).

[10a] A. C. Ling and J. E. Willard, *J. Phys. Chem.* **72**, 1918 (1968); [b]J. S. Hutzler, R. J. Colton and A. C. Ling, *J. Phys. Chem. Engng Data* **17**, 324 (1972).

[11] H. Tomioka, G. W. Griffin and K. Nishiyama, *J. Am. Chem. Soc.* **101**, 6009 (1979).

[12] H. Kristinsson and G. W. Griffin, *Ibid.* **88**, 1579 (1966).

[13] M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.* 1966 (1964).

[14] M. D. Cohen, *Angew. Chem. Int. Ed. Engl.* **14**, 386 (1975); see also I. C. Paul and D. Y. Curtin, *Accts. Chem. Res.* **6**, 217 (1973).

[15] H. Tomioka, Y. Ozaki, Y. Koyabu and Y. Izawa, *Tetrahedron Lett.* **23**, 1917 (1982).

[16] R. A. Moss and W. P. Wetter, *Ibid.* **22**, 997 (1981).

[17] H. Tomioka, S. Suzuki and Y. Izawa, *Chem. Lett.* 293 (1980).

[18] The possibility that atom abstraction may occur via a quantum mechanical tunneling mechanism in frozen mechanism in frozen matrices has been raised by Platz (ref. 27). In this case chlorine would be too massive to tunnel and hence be unreactive.

[19] J. Zayas and M. S. Platz, *Tetrahedron Lett.* **24**, 3689 (1983).

[20] Refs 2 and 24.

[21] H. Tomioka, Y. Ozaki and Y. Izawa, *Chem. Lett.* 843 (1982).

[22] N. J. Turro, J. A. Butcher Jr., R. A. Moss, W. Guo, R. C. Munjal and M. Fedorynski, *J. Am. Chem. Soc.* **102**, 7576 (1980).

[23] S. W. Benson, *Thermochemical Kinetics*. Wiley, New York (1968).

[24] H. Tomioka and Y. Izawa, *J. Am. Chem. Soc.* **99**, 6128 (1977). Similar results have been obtained with ethers and amines as solvent, see H. Tomioka, S. Suzuki and Y. Izawa, *Bull. Chem. Soc. Jpn.* **55**, 492 (1982).

[25] H. Tomioka, *J. Am. Chem. Soc.* **101**, 256 (1979).

[26] H. Tomioka, T. Miwa, S. Suzuki and Y. Izawa, *Bull. Chem. Soc. Jpn.* **53**, 753 (1980).

[27] M. S. Platz, V. P. Senthilnathan, B. B. Wright and C. W. McCurdy Jr., *J. Am. Chem. Soc.* **104**, 6494 (1982).

[28] H. Tomioka, S. Suzuki and Y. Izawa, *Chem. Lett.* 293 (1980).

[29] H. Tomioka, H. Okuno and Y. Izawa, *J. Chem. Soc. Perkin II* 603 (1980).

[30] H. Tomioka, M. Itoh, S. Yamakawa and Y. Izawa, *Ibid.* 1636 (1980).

[31] H. Tomioka, T. Inagaki, S. Nakamura and Y. Izawa, *J. Chem. Soc. Perkin I* 130 (1979).

[32] C.-T. Lin and P. P. Gaspar, *Tetrahedron Lett.* **21**, 3553 (1980).

[33a] V. P. Senthilnathan and M. S. Platz, *J. Am. Chem. Soc.* **102**, 7637 (1980); [b] V. P. Senthilnathan and M. S. Platz, *Ibid.* **103**, 5503 (1981); [c] B. B. Wright, V. P. Senthilnathan, M. S. Platz and C. W. McCurdy Jr., *Tetrahedron Lett.* **23**, 833 (1982).

[34a] H. Y. Wang and J. E. Willard, *J. Phys. Chem.* **83**, 3585 (1979); [b] D. D. Wilkey and J. E. Willard, *Ibid.* **64**, 3976 (1976); [c] S. Aditya, D. D. Wilkey, H. Y. Wang and J. E. Willard, *Ibid.* **83**, 599 (1979); [d] M. A. Long and J. E. Willard, *Ibid.* **74**, 1207 (1970).

[35] R. P. Bell, *The Tunnel Effect in Chemistry*. Chapman and Hall, New York (1980).

[36] R. J. LeRoy, H. Murai and F. Williams, *J. Am. Chem. Soc.* **102**, 2325 (1980).