cyclopropane. This is consistent with a direct attack of $HFCO_2$ or :CHF (obtained from decomposition of $HFCO_2$) upon the olefin.

$CHF{=}CH_2$ and $CH_2{=}CF_2$ ozonolyses do not yield epoxides and cyclopropanes.[2-5,9,10] In these cases there is evidence that indicates that the primary ozonides cleave preferentially to give H_2CO_2 and HFCO or F_2CO.[5,10] The primary ozonides of *cis*- and *trans*-CHF=CHF and $CF_2{=}CF_2$ cleave to produce $HFCO_2$ + HFCO and F_2CO_2 + F_2CO, respectively. $CHF{=}CF_2$ primary ozonide may cleave to give either $HFCO_2$ and F_2CO or F_2CO_2 and HFCO. It is possible that H_2CO_2 addition to an aldehyde is favored over epoxidation or addition to the olefin to produce cyclopropane. Hence, $CHF{=}CH_2$ and $CF_2{=}CH_2$ ozonolyses are more similar to those of small alkyl-substituted olefins in terms of the types of major products. The other fluorinated ethylenes must give $HFCO_2$ or F_2CO_2 and these species may not add to HFCO and F_2CO as readily. Therefore, other processes such as epoxidation or cyclopropane formation may become competitive and even dominate in the case of $CF_2{=}CF_2$. Further work is required to identify the intermediates involved in the formation of epoxides and cyclopropanes.

Acknowledgment is made to members of Dr. Potts's research group with help in obtaining NMR and mass spectra. We are also grateful to Peter Demou of the NSF NMR facility at Yale University and Dr. Herbert Schwartz of RPI for assistance in obtaining 200-MHz ^1H and ^{19}F NMR. We thank R. L. Kuczkowski and members of his research group for advice and helpful discussions. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Research Corp. for partial support of the research.

Registry No. 1,1-Difluoroethylene, 75-38-7; trifluoroethylene, 359-11-5; tetrafluoroethylene, 116-14-3; 1,1-difluoroethylene ozonide, 69932-17-8; trifluoroethylene ozonide, 86013-87-8; trifluoroethylene oxide, 2925-24-8; *cis*-1,2-difluoroethylene ozonide, 54892-64-7; *trans*-1,2-difluoroethylene ozonide, 54892-65-8; *cis*-1,1,2,3-tetrafluorocyclopropane, 49852-49-5; *trans*-1,1,2,3-tetrafluorocyclopropane, 49852-50-8; perfluoroethylene epoxide, 694-17-7.

Solid-State Chemistry, Kinetics, and Spectroscopy of 1,2-Diphenylpropylidene

Hideo Tomioka,* Norihiro Hayashi,[†] Yasuji Izawa,[†] V. P. Senthilnathan,[‡] and Matthew S. Platz*[‡,1]

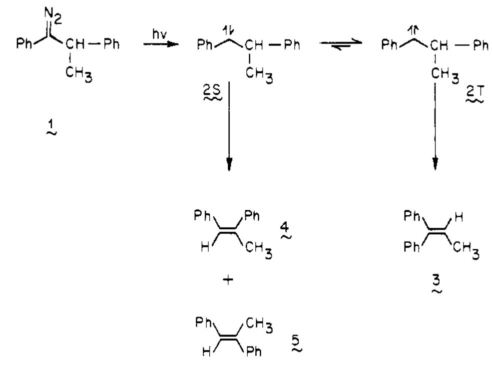
Contribution from the Chemistry Department of Industry and Resources, Mie University, Tsu, Mie, 514 Japan, and the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received October 14, 1982*

Abstract: Photolysis of diazo compound **1** at low temperatures produces the triplet ESR spectrum of carbene **2T**. The only kinetically important process of **2T** in glasses at low temperature is hydrogen atom abstraction from the matrix. Carbene **2T** is long lived in polycrystals. The products observed in polycrystals may be due in part to annealing a sample containing unreacted carbene. Studies of **2T** in perfluorinated matrices between −154 and −170 °C revealed that 1,2 hydrogen atom shifts do occur from the triplet (albeit slowly) by an unknown mechanism (Scheme I). Singlet carbene **2S** undergoes 1,2 hydrogen atom shifts without an appreciable product isotope effect. The chemistry and kinetics of both **2S** and **2T** in the solid state are strongly influenced by the matrix.

In the past few years several research groups have studied the chemistry of carbenes in polycrystalline solids and glasses at low temperature.[2] In the case of carbenes with triplet ground states there are profound differences between the chemistry observed in fluid solution at elevated temperatures (273–300 °C) and that obtaining in solids at −196 °C. Part of the change in chemistry can be attributed to the temperature difference. The product distribution obtained from carbenes responds to temperature variation because the activation parameters of singlet and triplet carbene processes are likely to be different. Furthermore, the equilibrium concentrations of the singlet and triplet carbenes (if equilibrium is achieved) will vary with temperature. In general, when one has a triplet ground state one observes a large increase in triplet chemistry (hydrogen atom abstraction–recombination and non-stereospecific cyclopropanation of alkenes) over singlet chemistry (intramolecular 1,2 hydrogen atom shift, stereospecific cyclopropanation, insertion into hydroxyl bonds) at the temperature of liquid nitrogen. Whether the rate of singlet–triplet equilibrium in a carbene is fast or slow relative to chemical reaction is a crucial mechanistic question. This question has been answered for a few systems.[3] However, it is quite possible that dramatic changes in temperature may alter the relative rates of non-radiative relaxation relative to chemical processes.

Temperature cannot be the sole determining factor, however. The solid-state environment exerts considerable control over matrix reactions. Tomioka, Griffin, and Nishiyama generated phenyl carbene from several precursors.[2e] The same chemistry from all

Scheme I



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[†] Mie University.

[‡] The Ohio State University.

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Table I. Glassy Matrix Decay Rate Constants for Carbene **2T**

matrix	temp, °C	k, $s^{1/2}$
2-MTHF	−196	0.013 ± 0.0002
	−186	0.041 ± 0.0011
	−183	0.066 ± 0.006
ethanol	−196	0.013 ± 0.001
	−183	0.048 ± 0.001
	−180	0.054 ± 0.003
ethanol-d_6	−196	0.0071 ± 0.0007
	−182	0.024 ± 0.001
	−179	0.059 ± 0.009
	−176	0.120 ± 0.02
diethyl ether	−196	0.013 ± 0.002
	−186	0.040 ± 0.002
	−183	0.071 ± 0.001
diethyl ether-d_{10}	−196	0.0066 ± 0.0006
	−182	0.031 ± 0.002
	−179	0.15 ± 0.01

Table II. Glassy Matrix Decay Rate Constants for Carbene **2T-*d***

matrix	temp, °C	k, $s^{1/2}$
2-MTHF	−196	0.014 ± 0.001
	−186	0.041 ± 0.004
	−183	0.062 ± 0.008
ethanol	−196	0.013 ± 0.001
	−186	0.030 ± 0.001
	−183	0.038 ± 0.003
diethyl ether	−196	0.016 ± 0.001
	−186	0.030 ± 0.001
	−183	0.071 ± 0.008

precursors was observed in solution; however, very different chemistry was observed in the solid at −196 °C. These workers observed that "Topochemical factors, i.e., contact of carbene center with the host molecules ... play an important role especially in the matrix reactions .... The fate of carbenes generated in a matrix may be predestined by site preference imposed upon the precursor". Several other examples of matrix control over solid-state carbene chemistry have been reported by Tomioka.[2e–i]

In 1980 Tomioka reported the temperature-dependent photochemistry of 1,2-diphenyl-1-diazopropane (**1**).[2k] It was found that there are three olefinic products formed in solution. As long as the reaction mixture was fluid, lowering the temperature increased the yield of phenyl migration product **3** at the expense of hydrogen migration products **4** and **5**. The products of 1,2 hydrogen shift are most likely derived from the singlet carbene. The phenyl migration product can be formed from either singlet or triplet carbene, or both spin states.[4] Upon lowering the reaction temperature past the freezing point, the phenyl migration product **3** was effectively suppressed. This was ascribed to the large unfavorable motion required to move a bulky phenyl group in the solid state. To more fully examine the solid-state chemistry of this system a series of kinetic and spectroscopic studies was undertaken. This approach has uncovered some hitherto unsuspected chemistry in this system, which further illustrates the complexities involved in reactions in polycrystals and glassy media.

Results and Discussion

Photolysis of diazo compound **1** (or **1-*d***) at −196 or −269 °C gives rise to an intense ESR spectrum of a triplet carbene $|D/hc| = 0.498$ cm^{-1}, $|E/hc| = 0.027$ cm^{-1}. The spectrum is assigned to **2** (or **2-*d***) on the basis of the similarity of the zero-field parameters observed to those of other alkyl-aryl carbenes.[5] The fact that **2** can be observed as a stable entity at −269 °C means that the triplet is the ground state, or within a few calories/mole of the ground state.

On the basis of the previously reported matrix product studies of **2**, one anticipated that the triplet should be indefinitely stable at −196 °C. However, in 2-methyltetrahydrofuran (2-MTHF), diethyl ether (ether), and ethanol glass the ESR spectrum of **2** rapidly decays at temperatures ≥−196 °C upon shuttering the light source (Table I). The kinetics are nonexponential as is common for reactions in disordered solids.[6] This arises from site differences within the matrix. Matrix photolysis of diazo compound **1** produces a distribution of carbenes in different environments. Different carbenes in the matrix will have different orientations relative to the host molecules and the photoextruded nitrogen, and will have different intra- and intermolecular reaction kinetics. The ESR kinetics are summed over many sites with different rate constants. The products obtained in the matrix reactions must also reflect the chemistry of many diverse sites. Furthermore, the chemistry of different sites in the same matrix may be quite different. There may exist sites in the matrix in which the triplet carbene reactions are too fast to resolve by conventional ESR. Therefore, it is important to bear in mind that the conclusions to be drawn from the ESR kinetics are valid for only those sites that can be time resolved. The latter represent a subset of unknown proportion of the total yield of triplet carbene in the matrix.

It was empirically determined that the decay of triplet carbene **2** in glassy ethanol, ether, or 2-MTHF follows a $t^{1/2}$ rate law. This unusual rate law is quite common for reactions in glasses. It has been observed previously in glasses for free radicals,[7] carbenes,[8] and excited states.[9] Förster has studied energy transfer in the absence of diffusion in considerable detail. When energy transfer occurs by a dipole–dipole mechanism the rate of energy transfer is dependent upon the separation of the donor and acceptor molecules. When the distribution of molecules is heterogeneous (as in a polymer film) there will be a wide variation of energy transfer rate constants within the sample, reflecting the wide variation in separation between various donor and acceptor pairs. Upon assuming a distribution function for the various distances between donor and acceptor pairs Förster specifically derived rate laws encompassing a square root of time dependence. There is an obvious physical similarity between energy transfer and carbene reactions in amorphous solids. In both cases one has an ensemble of reactant pairs, each associated with a unique rate constant dependent upon the local environment. This does not mean that Förster's proof is applicable to carbenes. The square root of time–rate laws observed for carbenes and radicals has not yet been successfully modeled. There are numerous reports of exponential kinetic rate laws being followed in glasses (such as phosphorescence lifetimes[9d]) in the literature.

The kinetic data of Tables I and II are reported in the matrix units of seconds$^{-1/2}$. It is not our intention here to associate a rate constant in units of second$^{-1/2}$ with a specific molecular event. Instead, the second$^{-1/2}$ units is the most precise way of reporting our data, and it provides a qualitative guide for comparing the gross reactivity of triplet carbene **2** in different glasses.

The chemical reaction responsible for the ESR decay process is revealed by kinetic isotope effects. Within experimental error, deuteration α to the carbene center produces no kinetic isotope effect in ethanol, ether, or 2MTHF (Table II). This argues against

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Table III. The Product Distribution Obtained From Carbene **2** as a Function of Temperature[d]

matrix	carbene	temp, °C	3	4	5	6
ether	**2**	20	26.3	45.7	28.0	0
	2	0	27.3	41.2	31.5	0
	2	−196	1.0	40.3	26.2	32.5
	2-*d*	0	44.6	28.7	26.7	0
	2-*d*	−196	6.9	38.3	19.5	35.3
ether-d_{12}	**2**	0	28.5	39.2	32.3	0
	2	−196	3.5	49.6	29.2	17.7
	2-*d*	0	48.0	27.3	24.7	0
	2-*d*	−196	7.9	50.8	26.5	14.8
ethanol	**2**	20	3.5	22.9	13.4	60.2[a]
	2	−196	1	43.0	25.3	6.8[a] (23.9)[c]
methylcyclohexane	**2**	20	21.5	39.1	39.4	0
	2	−196	3.1	58.5	6.5	31.9[c]
benzene	**2**′	20	26.5	43.6	29.9	0
	2	−196	8.2	55.4	27.7	8.7[c]
n-hexane	**2**	20	27.8	41.1	31.1	0
	2	−196	10.3	45.7	39.1	14.9[c]

[a] OH insertion. [b] CH insertion. [c] A mixture of CH insertion isomers. [d] The experimental error is ±2%.

Table IV. Polycrystalline Matrix Decay Rate Constants for Carbene **2T**

matrix	temp, °C	k, $s^{-1/3}$
benzene	−170	0.061 ± 0.003
	−167	0.064 ± 0.003
	−164	0.051 ± 0.002
benzene-d_6	−170	0.068 ± 0.003
	−167	0.063 ± 0.002
	−164	0.047 ± 0.002
hexafluorobenzene	−164	0.053 ± 0.002
	−159	0.063 ± 0.001
	−154	0.073 ± 0.003

a 1,2 hydrogen shift reaction in the triplet carbene in the low-temperature glasses. However, perdeuteration of the ethanol or ether glasses leads to a substantial rate retardation (Table I). The kinetic data point to intermolecular hydrogen atom abstraction as the triplet decay mechanism in glassy matrices. Indeed, a reexamination of the chemistry of **2** at −196 °C reveals a substantial yield of matrix-incorporated products **6** (see Table III) which can result from the collapse of radical pair **7**. The presence of the double hydrogen atom abstraction product (1,2-diphenylpropane) was not detected. The observed ESR signal decay can be associated with at most 30.7% of the chemistry observed in the ethanolic glass, and 32.5% of the chemistry in ether at −196 °C. The involvement of **2T** in the products may be much less than these percentages as **2S** may insert into CH bonds of the matrix. The presence of large amounts of **4** and **5** in the matrix product distribution is most easily explained by the rapid reaction of singlet **2S** prior to intersystem crossing.[10]

The decay of **2T** was examined next in the polycrystalline matrices benzene, methylcyclohexane, cyclohexane, and hexafluorobenzene (Table IV). The consumption of **2T** in the solids at −196 °C is orders of magnitude slower than that observed in glasses. In fact, at −196 °C there is essentially no signal decay over several days in the polycrystals. The increased yield of phenyl migration product **3** in polycrystals relative to that in glasses may have a trivial explanation. Exhaustive photolysis of diazo compound **1** in a polycrystal may produce triplet carbene **2T** which is not completely consumed at low temperature. Upon thawing the sample the triplet carbene can undergo phenyl migration once the environment becomes fluid.

Table V. Polycrystalline Matrix Decay Rate Constants for Carbene **2T**-*d*

matrix	temp, °C	k, $s^{-1/3}$
benzene	−170	0.049 ± 0.002
	−167	0.040 ± 0.002
	−164	0.040 ± 0.002
benzene-d_6	−170	0.057 ± 0.002
	−167	0.054 ± 0.002
	−164	0.054 ± 0.002
hexafluorobenzene	−164	0.035 ± 0.003
	−159	0.049 ± 0.002
	−154	0.060 ± 0.003

It is possible to measure the decay of **2T** upon warming the sample 25–40 °C above the boiling point of nitrogen. It was empirically determined that in benzene, benzene-d_6, and hexafluorobenzene polycrystals, a $t^{1/3}$ kinetic order was followed. This rate law has been observed previously for triplet carbenes in polycrystals.[7] It reflects the increased severity of site problems in polycrystals relative to glasses. The data of Tables IV and V are reported in matrix units of seconds$^{-1/3}$ in the interest of precision only. The decay kinetics in cyclohexane, cyclohexane-d_{12}, and methylcyclohexane did not follow any simple rate law, hence, it was not possible to analyze the data in any meaningful way.

There are three significant differences between the kinetics of **2T** in glasses (Table I and II) and in polycrystals (Table IV and V). First, at −196 °C, **2T** is orders of magnitude more reactive in glasses which have abstractable hydrogens (ether and ethanol—Table I) than in crystals which are poor hydrogen atom donors (benzene and hexafluorobenzene—Table IV). Second, the fast reaction in glasses is retarded upon isotopic substitution of the glass (Table I). The slow reaction of **2T** in benzene is not further retarded in benzene-d_6 (Table IV). Third, the fast reaction in glasses has the same rate for both **2T** and its deuterated modification **2T**-α-*d* (Table II). The slow reaction in polycrystals displays a substantial carbene α-*d* isotope effect.

In ether glass **2T** can decay intermolecularly by reaction with the matrix, or intramolecularly to give olefins **4** and **5**. In hexafluorobenzene, the intermolecular hydrogen-transfer route is not possible, hence intramolecular hydrogen migration can become dominant. The observation of a substantial α-deuterium kinetic isotope effect in hexafluorobenzene strongly supports the assignment of the decay reaction in this matrix as intramolecular hydrogen migration. It does not seem reasonable that changing the matrix from hexafluorobenzene to ether should increase the rate of the intramolecular hydrogen shift by orders of magnitude at −196 °C. There is also no reason to expect that changing the matrix from C_6F_6 to ether should cause the α-*d* isotope effect to disappear in the intramolecular route. For these reasons we feel that the 1,2 hydrogen migration from **2T** in ether or ethanol at −196 °C is too slow to be of any consequence. The decay of **2T** under these conditions is believed to be purely intermolecular.

It is apparent that the 1,2 hydrogen shift does occur in triplet carbenes, albeit slowly, and only when other processes (phenyl migration, H atom abstraction) are suppressed by an inert polycrystalline environment. The mechanism of this process is not revealed by the limited kinetic data. It is conceivable that the reaction occurs by the slow formation of **2S** retroactivity from **2T**, followed by a rapid hydrogen shift. A surface-crossing mechanism is also possible. The uncertainty is characteristic of spin-forbidden reactions, in general, at the present time.[11]

A more complete mechanistic picture is given in Scheme II. It is further clarified by the results of a carbene isotope, and matrix isotope product study. Deuteration α to the carbene center leads to very small changes in the product composition in either ether or ether-d_{10}. The total yield of hydrogen shift products changes from 66.5 to 57.8% in ether and from 78.8 to 77.3% in ether-d_{10},

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(10) A referee has suggested that olefins **3**, **4**, and **5** may be formed (in part) concerted with loss of nitrogen, without the intervention of carbenes. We cannot rule out this possibility. However, some carbene must be formed as **2T** can be detected by ESR and by its reaction with the matrix.

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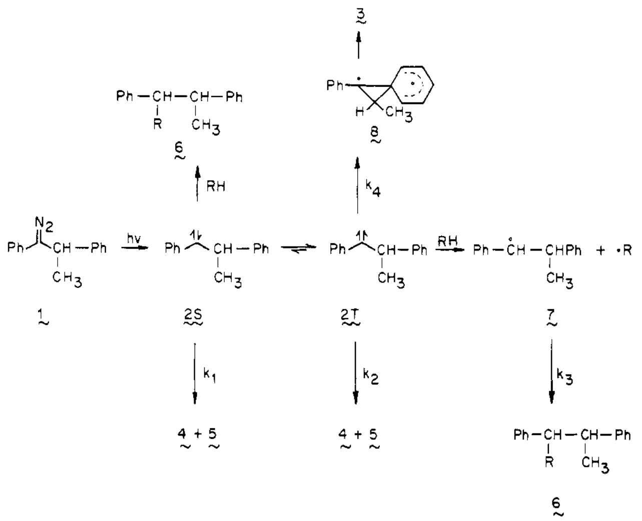
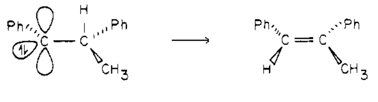
Scheme II



the latter change being within the experimental error (±2%). In the case of the ether glass, α deuteration leads to a negligible increase in matrix insertion product (Table III). The kinetic studies performed in polycrystals indicated that the triplet 1,2 hydrogen shift is too slow to be of any consequence in ether or ether-d_{10}. This means that the small to zero product isotope effect to hydrogen shifting at −196 °C can be completely associated with singlet **2S**.[10] This is in startling contrast to the solution results obtained in ether at 0 °C. In both ether and ether-d_{10}, deuteration α to the carbene center substantially increases the yield of phenyl migration product **3** at the expense of deuterium migration products **4** and **5**. The solution results indicate that there is an isotope effect to the 1,2 hydrogen shift reaction. The discrepancy can be resolved by recourse to a matrix effect. First, the competing intramolecular phenyl rearrangement is prohibited by the large motion required to migrate a phenyl group in the matrix. Second, the chemistry of singlet **2S** be it ISC to **2T**, 1,2 hydrogen shift, or insertion into the matrix may be entirely predestined by the local matrix site, regardless of whether hydrogen or deuterium is α to the carbene center.

Deuteration of the ethereal matrix leads to larger changes in the chemistry of **2** than deuteration of the carbene at low temperature. A comparison of **2** (or **2**-*d*) in ether vs. ether-d_{10} (Table III) reveals that the yield of matrix incorporated product **6** is cut roughly in half while the yields of hydrogen atom shifted products **4** and **5** are increased. It is true that ESR kinetics show there is an isotope effect on the reaction of **2T** with the matrix. However, the ESR studies indicate that it is the only reaction of **2T** in ether-d_{10} at −196 °C. The kinetics of 1,2 hydrogen shift via **2T** are too slow to be important in ether-d_{10}.[12] Once **2T** is formed in ether-d_{10} its eventual fate is the formation of matrix-incorporated products. Although deuteration can affect the rate of this process it cannot affect the eventual yield of **6**. The origin of the product isotope effect must lie elsewhere.

A simple interpretation of the product isotope effect observed upon deuteration of the matrix is that some of the matrix-incorporated product **6** arises from the singlet carbene in competition with hydrogen shift. In fluid solution neither **2S** or **2T** react with the solvent in competition with intramolecular routes. The ideal geometry for 1,2 shift has the empty p orbital eclipsing the migrating hydrogen.[13] A solid-state matrix can retard this process by preventing the motion needed to achieve a good alignment, or by retarding the motions of both of the phenyls and of the methyl group, which accompany hydrogen migration.



The product matrix isotope effect can be simply explained if there are some sites in which singlet **2** partitions between 1,2 shift and insertion into a matrix C–H bond, the latter process having a finite isotope effect. If this view is correct than the ESR detected triplet carbene **2T** corresponds to defects in the matrix, those matrix sites in which the intramolecular rearrangements of **2S** are retarded by the local environment. Presumably there is no conformation change upon intersystem crossing, therefore, intramolecular 1,2 hydrogen atom shifts in the triplet carbene are not only spin forbidden but conformationally or matrix forbidden as well![12] The kinetic data of Tables IV and V probably reflect the rate at which triplet **2** moves into a conformation permissive of the 1,2 hydrogen shift reaction. It would appear that solid-state ESR kinetic studies of unimolecular reactions of triplets will reveal more about environmental factors than about the desired reaction. Attempts to interpret such data as an unfettered gas or solution phase process should be regarded with caution.

Conclusions

The ground state of carbene **2** is the triplet. ESR can be used to monitor the kinetics of the decay of **2T** in glasses and polycrystals. The only kinetically important process of **2T** observed in glasses is hydrogen atom abstraction from the matrix.[11] The decay of **2T** in polycrystals is very slow. The higher yields of phenyl migration product **3** found in polycrystals relative to glasses results from thawing matrices containing unreacted triplet. Studies in perfluorinated matrices reveal that 1,2 hydrogen shifting can occur from the triplet (albeit slowly) by an unknown mechanism. Singlet carbene **2S** undergoes 1,2 hydrogen atom shifts without an appreciable product isotope effect in the matrix. A more substantial product isotope effect is observed on the singlet 1,2 hydrogen shift in fluid solution. In fluid, non-hydroxylic solvents, the chemistry of **2S** and **2T** is purely unimolecular. In low-temperature matrices, each spin state reacts with the matrix with an isotope effect.

Experimental Section

The ESR system used in the kinetic studies has been described elsewhere. The isotopically labeled solvents were obtained from Merck and used without purification. Kinetic studies were run with 0.1 M diazo compound **1**.

Product Analyses. All irradiations for product analyses were conducted with use of a Halos 300-W high-pressure mercury lamp with a water-cooled jacket. In a typical procedure, 0.005 mmol of the diazomethane was added to 2.0 mL of the appropriate solvent in Pyrex tubes. The sample was then degassed by using three freeze–thaw cycles, and the sample tube was sealed under vacuum. The tube was suspended in a transparent Pyrex Dewar flask filled with coolant and irradiated until all diazomethane was destroyed. A Corning CS-052 filter (cut off at 350 nm) was used in order to avoid product isomerization. Control experiments ruled out the interconversion of the product during irradiations and also showed that no reaction occurred in the absence of light in the range of temperature studied. The diazomethane was prepared just before use. That no olefins were present before irradiation was checked by NMR. The product identification and yields were conveniently determined by standard GC (Silicone OV-17 on Diasolid L, 170–210 °C, 30 °/min) and GC-MS (Shimadzum GC-MS 1000 spectrometer) techniques. Authentic olefins (**3**,[15] **4**,[15] and **5**[16]) were prepared according to the literature procedures.

1,2-Diphenyl-*2*-*d*-diazopropane. The unlabeled diazo compound has been prepared previously.[14] Four grams of 1,2-diphenylpropanone was dissolved in 10 mL of ethanol-O-d (Merck). To this was added 2 drops of 40% NaOD in D_2O (Aldrich). The solution was stirred under a nitrogen atmosphere for 30 min. At this time 2 drops of D_3PO_4 (Merck) was added to neutralize the basic solution. The solvent was removed

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[12] It is conceivable that there are matrix sites containing triplet **2** which react too rapidly to be detected by CW ESR. We cannot rule out this possibility.

[13] The 1,2 hydrogen shift has been studied theoretically. The calculations indicate a large barrier in the triplet state and essentially no barrier to the singlet reaction. (a) Atmann, J. A.; Csizmadia, I. G.; Yates; *J. Am. Chem. Soc.* **1975**, *97*, 5217. (b) Schaefer, H. F. *Acc. Chem. Res.* **1979**, *12*, 288. (c) Conrad, M. P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1978**, *100*, 7829.

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under vacuum, and the ketone was vacuum distilled. NMR analysis of the ketone showed 80% deuterium incorporation. Repetition of the above procedure gave a sample greater than 95% enriched in deuterium. Deuterated ketone (2.5 g) and 5.0 g of (*p*-toluenesulfonyl)hydrazide were dissolved in a minimal amount of ethanol-O-*d*. The solution was refluxed under a nitrogen atmosphere for 2 h. The solution was cooled to room temperature. Upon standing the product (*p*-toluenesulfonyl)hydrazone precipitated (yield 4 g), mp 151–155 °C. Deuterated (*p*-toluenesulfonyl)hydrazone (0.1 g) was dissolved in 5 mL of 1,4-dioxane. To this was added 5 mL of 40% NaOD in D_2O. The two-phase reaction was refluxed under nitrogen until the pink diazo color was observed. After being cooled to room temperature, the pink dioxane layer was separated, and the solvent removed under vacuum. The residue was extracted into hexane. The hexane solution was dried over sodium sulfate and filtered and the solvent removed to give the residue 1,2-diphenyl-*2-d*-diazopropane product.

1,2-Diphenyl-1-hydroxypropyl Ethyl Ether. 1,2-Diphenyl-1-propanol[17] was added to a stirred suspension of 2.08 g (50 mmol) of finely powdered sodium hydroxide in 10 mL of dimethyl sulfoxide. To the resulting mixture was added 31 g (20 mmol) of ethyl iodide at room temperature, and the solution was stirred overnight. After dilution with 25 mL of water the product was extracted with ether. The organic phase was washed with water and dried over anhydrous sodium sulfate, and the volatile solvents were removed. The residual oil was then purified by passing it through a short silica gel column: NMR (CCl_4) δ 1.12 (t, J = 7 Hz, 3 H), 1.33 (d, J = 7 Hz, 3 H), 2.74∼2.96 (m, 1 H), 3.00–3.44 (m, 2 H), 4.15 (d, J = 7 Hz, 1 H), 6.88–7.32 (m, 10 H).

3,4-Diphenyl-2-pentanol. Phenylacetone (1.34 g, 10 mmol) was added to a stirred suspension of NaOH (0.5 g, 21 mmol) in 5 mL of dry benzene and 50 mL of anhydrous dimethylformamide at 5–10 °C. The mixture was stirred for 20 min and treated dropwise at 10 °C with α-phenethyl bromide (7.4 g, 40 mmol). The mixture was warmed gradually to room temperature and heated 5 h at 50–60 °C. The cooled mixture was diluted with 5 mL of alcohol and water and the organic phase was washed with aqueous $NaHSO_3$ and water and dried over anhydrous Na_2SO_4. Evaporation of solvents given crude 3,4-diphenylpentan-2-one (1.95 g, 82%), which was used in the reduction without further purification. NMR ($CDCl_3$) δ 3 H at 0.98 (d, J = 7 Hz) and 1.32 (d, J = 16 Hz), 3 H at 1.80 (s) and 2.06 (s), 1 H at 3.57 (q, J = 7 Hz), and 3.42 (q, J = 7 Hz), 1 H at 3.85 (s) and 3.96 (s), 10 H at 7.05∼7.44 (m).

To a stirred slurry of powdered lithium aluminum hydride (0.375 g, 10 mmol) in anhydrous ether (10 mL) was added a solution of 1.95 g (8.2 mmol) of 3,4-diphenylpenta-2-one in 5 mL of anhydrous ether at a rate that maintains gentle refluxing of the solvent. After the addition was complete, the reaction solution was boiled under reflux for an additional 30 min and then allowed to cool. The complex and excess $LiAlH_4$ were hydrolyzed by addition of 1 mL of water and the resulting reaction mixture was poured into 30 mL of cold aqueous sodium bicarbonate and dried over magnesium sulfate. Evaporation of solvents gave crude 3,4-diphenylpentan-2-ol (1.78 g, 91%), which was purified by passing it through a short silica gel column: NMR (CCl_4) δ 3 H at 0.77 (d, J = 6 Hz) and 1.18, 3 H at 1.02 (d, J = 6 Hz) and 1.38 (d, J = 6 Hz), 1 H at 2.62 (t, J = 6 Hz) and 3.16 (t, J = 6 Hz), 1 H at 2.40–2.78 (m) and 3.12, 3.44 (m), 1 H at 3.44, 3.76 (m) and 4.08, 4.16 (m), 10 H at 6.80, 7.32 (m).

3,4-Diphenyl-2-hydroxypentyl Ethyl Ether. The procedure used was identical with that used with 1,2-diphenyl-1-hydroxypropyl ethyl ether. One gram (4.2 mmol) of alcohol was treated with ethyl iodide in the presence of NaOH to afford 0.88 g (79%) of product. NMR (CCl_4) δ 0.75 (d, J = 6 Hz, 3 H), 1.20 (t, J = 6 Hz, 3 H), 1.40 (d, J = 6 Hz, 3 H), 2.84 (t, J = 6 Hz, 1 H), 3.10–3.72 (m, 2 H), 3.74, 4.06 (m, 1 H), 4.06, 4.44 (m, 1 H), 6.84–7.36 (m, 10 H).

1,2-Diphenylpropane. A mixture of amalgamated zinc (prepared from 20 g of mossy zinc and 1 g of mercuric chloride), 15 mL of water, 15 mL of concentrated hydrochloric acid, and 2.1 g (10 mmol) of 1,2-diphenyl-1-propanone was refluxed vigorously for 10 h. A 2-mL portion of concentrated hydrochloric acid was added every 3 h during the heating period. After the reaction mixture has been cooled to room temperature, the solution was decanted from unchanged zinc amalgam, saturated with sodium chloride, and extracted with ether. Removal of the solvent yielded crude 1,2-diphenylpropane (1.8 g, 90%). NMR ($CDCl_3$) δ 1.22 (d, J = 6 Hz, 3 H), 2.76, 1.34 (m, 1 H), 2.85 (d, J = 6 Hz, 2 H), 6.92–7.36 (m, 10 H).

1,1,2-Triphenylpropane was prepared as described in the literature.[18]

The individual CH insertion products with hexane and methylcyclohexane were not synthesized. These products were identified by exact mass measurement.

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Registry No. 1, 41683-70-9; **6** (R = H), 5814-85-7; **6** (R = OH), 28795-94-0; **6** (R = OEt), 85939-93-1; 2-MTHF, 96-47-9; D, 7782-39-0; H, 1333-74-0; diethyl ether, 60-29-7; ethanol, 64-17-5; methylcyclohexane, 108-87-2; benzene, 71-43-2; *n*-hexane, 110-54-3; 1,2-diphenylpropanone, 2042-85-5; phenylacetone, 103-79-7; α-phenethyl bromide, 585-71-7; 3,4-diphenylpentan-2-one, 33525-08-5; 3,4-diphenyl-2-pentyl ethyl ether, 85939-94-2; 1,2-diphenylpropylidene, 50462-70-9; 3,4-diphenylpentan-2-ol, 85939-95-3.

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