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CARBENES IN MATRICES: REACTIONS AND REARRANGEMENTS

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ABSTRACT

Carbenes and silylenes with a variety of substituents have been isolated and characterized in low temperature matrices Reactions of these species with small molecules, especially $^3O_2$, have been studied The structure of the primary addition products as well as the reactivity as a function of the spin-state (triplet T or singlet S) is discussed

INTRODUCTION

The reactivity and selectivity in carbene reactions is controlled by the spin state from which the reaction occurs According to the Skell–Woodworth rules [1] singlet and triplet carbenes can be differentiated by studying the products obtained in carbene reactions. Thus singlet carbenes add stereospecifically to olefins and insert preferentially into O–H bonds but react only very slowly with molecular (triplet) oxygen On the other hand triplet carbenes yield non-stereospecific cycloaddition products, insert into C–H bonds by an abstraction recombination mechanism and are readily oxidized by molecular oxygen A prerequisite for this is a large singlet–triplet gap ΔG_{ST}, which prevents the thermal excitation of low lying electronic states of different spin multiplicity, or a very small rate for the S–T isomerization k_{ST}

Recently the Skell–Woodworth rules have been challenged by the observation of formally "spin forbidden" reactions [2] Time resolved studies by Griller, Scaiano and co-workers demonstrate that triplet carbenes, like diphenylmethylene or fluorenylidene, insert into the OH-bond of methanol to give ethers [3] or react with nitriles [4] or ketones [5] to form ylides These results were obtained in solution at room temperature with nanosecond time resolution The observation of singlet chemistry from triplet carbenes can be explained either by rapid thermal population of excited singlet states [6, 7] or by the

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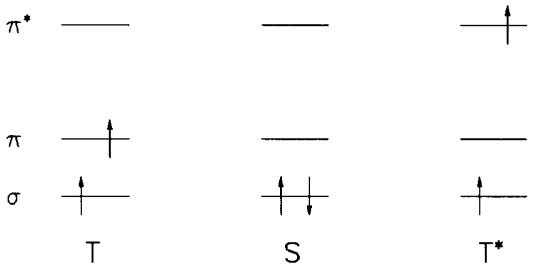
mixing of singlet and triplet states during the course of the reaction [2] The conclusion of these experiments was that in cases where ΔH_{ST} is small changes in reaction conditions largely affect the reactivity and it is difficult to apply the Skell–Woodworth rules [2]. When ΔG_{ST} is large, pure triplet reactivity is observed for triplet ground state carbenes, as is predicted by the Skell–Woodworth rules.

In low temperature (4–77 K) matrices only the ground state of the carbene is populated if ΔG_{ST} is larger than a few tenths of a kilocalorie. This technique allows free carbenes to be characterized by various spectroscopic techniques (IR, UV/vis, fluorescence, ESR). Both reactive matrices (organic glasses) (for a review see ref 8) and inert gas matrices doped with the reactant have been used to study carbene reactions. Due to the strong absorption of the solvent it is generally not possible to obtain IR spectra in organic glasses

Trozzolo et al. [9, 10] used organic glasses to obtain UV/vis, fluorescence, and ESR spectra of substituted diphenylmethylenes. Even at low temperature the triplet carbenes abstract H atoms from the solvent (organic glass) to give radicals [9, 10]. In solid alcohols some triplet carbenes yield both products of the formal C–H and O–H insertion [11, 12] and thus singlet reactivity is observed from triplet ground state carbenes (in violation of the Skell–Woodworth rules). The temperature dependence of product distribution was explained by special effects of alcohol matrices. Recently Platz and co-workers [13] demonstrated that many of these special matrix effects are caused by the prolonged lifetime of carbenes in alcohol matrices (several minutes or hours compared to nanoseconds or microseconds in liquid alcohols). In organic glasses carbenes are no longer short lived and secondary photolysis produces electronically excited triplet carbenes which react similarly to singlet carbenes. The similarity of excited triplet carbenes to singlet carbenes (rapid reaction with methanol) has also been established by experiments with picosecond time resolution [14].



An explanation for the singlet reactivity of excited triplet carbenes based on a simple molecular orbital scheme was presented by Eisenthal et al. [7] In the triplet ground state (T) both the nonbonding σ and π orbital are occupied with one electron. In the excited triplet state (T*) one electron is moved from the nonbonding π to an antibonding π^* orbital ($\pi \rightarrow \pi^*$ transition) resulting in an empty low-lying π orbital This low-lying π orbital is also responsible for some of the chemistry of singlet carbenes (S)

It is thus essential to differentiate between thermal and photochemical carbene reactions This can be achieved best by using inert gas (mainly Ar or N_2) matrices In these matrices carbenes are stable as long as intramolecular rearrangements are not possible Carbenes are produced in a photochemical step (irradiation at 10 K) from their matrix isolated precursors (diazo compounds or diazirines) The thermal reaction is induced by doping the matrix with a reactant and annealing at a temperature where the diffusion of components in the matrix is rapid This technique allows reactions in inert gas matrices to be followed by IR spectroscopy The disadvantage of Ar and N_2 matrices is that the upper limit of the temperature at which reactions can be observed is 45–50 K (rapid evaporation of the matrix) and that only small molecules diffuse rapidly enough in inert gases to give reactions

Several formally spin forbidden reactions in inert gas matrices have been reported The thermal reaction of triplet carbenes and CO to give ketenes has been observed for many carbenes and is of diagnostic importance to prove the presence of a free carbene [15] Recently the spin allowed reaction of silylenes and CO has also been observed [16] However, the low temperature reaction of (singlet) phenylchloromethylene (**7**) with $^3O_2$ to produce a carbonyl oxide has been reported [31], while laser flash studies at room temperature indicated no reactivity [2]

A systematic study of the influence of spin on the low temperature reactivity of carbenes has not been carried out We therefore thought it important to compare the reactivity of a variety of carbenes and silylenes with small molecules

EXPERIMENTAL METHODS

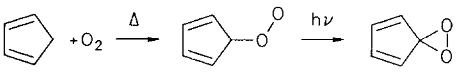
Matrix experiments were performed by standard techniques [17] using an Air Products CSW-202 Displex closed cycle helium cryostat In most experiments Ar was used as matrix material Kr or Xe was used if annealing at higher temperature was required or the influence of heavy atoms was of interest Carbenes were produced by irradiating matrix isolated diazo compounds or diazirines. Reactions were induced by doping the matrix with O_2 or CO_2, irradiating at low temperature (10 K), and then annealing at higher temperature when the diffusion of matrix isolated species becomes rapid (30–45 K)

By carefully controlling the matrix temperature it was possible to differentiate between diffusing particles of different size [18] Two types of annealing experiments have been performed In "free warm-up" experiments the cryostat was switched off and the matrix allowed to warm from 10 K to a certain temperature The rate of the temperature rise was 1–2 deg min^{-1} (depending on the absolute temperature) and was highly reproducible After reaching the desired temperature the matrix was quickly cooled to 10 K Alternatively, the temperature of the matrix was controlled by a heating element in combination with a silicon diode sensor and a Lake Shore temperature controller (for experimental details see ref 26)

IR spectra were recorded on a Perkin Elmer 580 A or a Bruker IFS 66 (FT-IR) spectrometer The resolution was generally 2 cm^{-1} on the PE 580 and 1 cm^{-1} on the IFS 66. UV/vis spectra were obtained on a Cary 17 D instrument, and luminescence (fluorescence and chemiluminescence) spectra on a laboratory built instrument based on a Princeton Applied Research OMA II detector (videcon) (for details see ref. 26)

REACTIONS OF CARBENES AND SILYLENES WITH $^3O_2$

The reactions of cyclopentadienylidene **1** and related carbenes with $^3O_2$ in inert gas matrices (Ar or N_2) have been investigated by Chapman and Hess [19–21] and by Dunkin and co-workers [22, 23]. Both groups reported different spectra for the primary adduct In 1986 Dunkin and Shields [23] were able to prove by isotopic labelling that the primary oxidation product of **1** is cyclopentadienone *O*-oxide (**2**) which easily rearranges to the dioxirane **3**



1 2 3

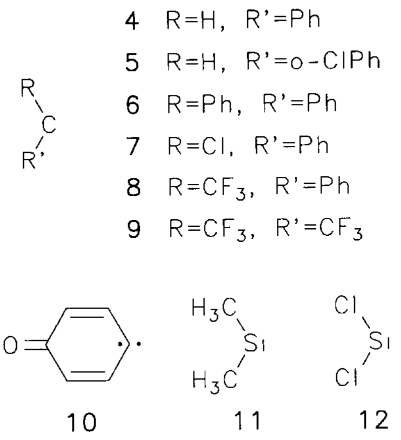
Our experiments were designed to gain some insight into the following questions:

(i) How does the spin state of the carbene influence reactivity with $^3O_2$? The conclusion from laser photolysis experiments was that singlet carbenes do not react with $^3O_2$ Does the reactivity in low temperature matrices differ from room temperature reactivity?

(ii) What is the structure of the primary oxidation products? Possible primary adducts are carbonyl *O*-oxides ("end-on" adducts) or dioxiranes ("side-on" adducts).

(iii) During the thermal oxidation of free carbenes an intense chemiluminescence is frequently observed What is the mechanism leading to the emission of light?

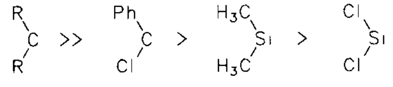
The oxidation of a variety of free carbenes and silylenes (Scheme 1) in O_2-doped Ar matrices has been examined [24–28]. In this series phenylchlorocarbene **7** and the silylenes **11** [29] and **12** [30] (Scheme 1) have singlet ground states, all other carbenes have triplet ground states



10 11 12

Scheme 1

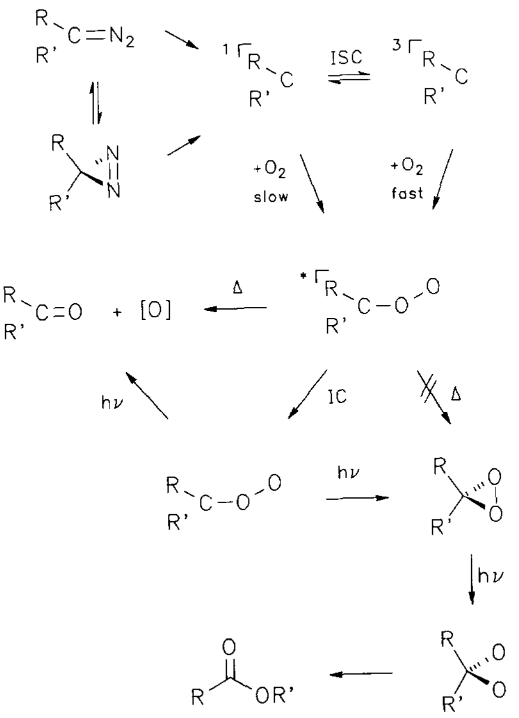
Experiments with standardized conditions (0.5%, 1%, 2% O_2 in Ar, free warm-up to 42 K) have been performed. Although it was not possible to measure absolute kinetics (because of the problem of measuring concentrations in matrices) the relative order of reactivity of the compounds in Scheme 1 has been obtained.



4-6, 8-10 7 11 12

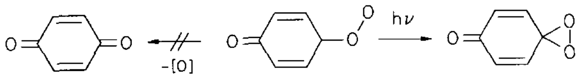
There is no observable difference in the reactivity of triplet carbenes, the reaction is controlled by the diffusion of $^3O_2$ in solid Ar. One "warm-up" cycle in a 1% O_2-doped Ar matrix completely converts the carbenes to the oxidation products. Phenylchloromethylene (**7**) with a singlet ground state shows a much lower reactivity even in 5% O_2 doped Ar matrices [31]. Several hours of annealing at 35 K is required for a partial conversion under conditions where triplet carbenes react completely within several minutes. While dimethylsilylene (**11**) reacts slowly at still higher temperatures [29], dichlorosilylene (**12**) shows no thermal reactivity even in pure O_2 matrices at temperatures where the matrix evaporates ($T=45$ K) [30]. Thus it is possible to isolate **12** in pure O_2 matrices. If **12** is generated in the gas phase under conditions of flash vacuum pyrolysis (FVP), no oxidation is observed even at 800°C, while dimethylsilylene (**11**) is oxidized almost completely under the same conditions. Visible light irradiation of **11** leads rapidly to the formation of an oxidation product. Presumably the photooxidation is induced by irradiation into a contact charge-transfer absorption (CCT-band of $\mathbf{11}\cdots O_2$).

In all cases the primary O_2-adducts of carbenes are carbonyl *O*-oxides (Scheme 2). These elusive species are highly labile towards long-wavelength irradiation ($\lambda=630$ nm [23, 24, 27, 28, 31] and rearrange to give dioxiranes or split off O atoms to give carbonyl compounds.



Scheme 2

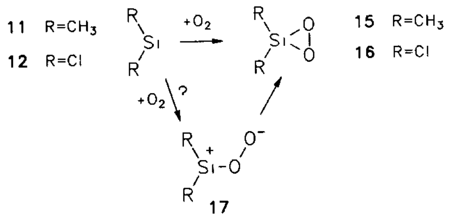
The ratio of dioxiranes to carbonyl compounds depends much on the substituents at the carbonyl O-oxide carbon atom Hydrogen substituents lead to O atoms and carbonyl compounds (the phenylmethylene/O_2 system is a highly efficient source of atomic oxygen [24b, 25]) while quinone *O*-oxide **13** leads exclusively to dioxirane **14** [28].



13 14

This chemistry is in accord with spectroscopic evidence and theoretical calculations which relate the frequency of the O–O stretching mode (and thus the stability of the O–O bond) to the electron withdrawing or donating capability of substituents [32] Electron withdrawing groups stabilize the O–O bond (π acceptors being more effective than σ acceptors) while electron donors destabilize the O–O bond in carbonyl *O*-oxides [32]

The oxidation of silylenes **11** and **12** leads directly to dioxasiliranes **15** and **16** [29, 30] According to ab initio calculations the barrier of isomerization of silanone *O*-oxide is 6.5 kcal mol^{-1} [29] whereas that of carbonyl *O*-oxide is 22 8 kcal mol^{-1} [33] In both cases the cyclization is highly exothermic (31 3 and 63 8 kcal mol^{-1}, respectively). This explains the difficulties in observing silanone *O*-oxides **17** formed in exothermic reactions. In contrast to our work is the observation by Ando and co-workers [34] that dimesitylenesilylene adds O_2 to give the corresponding silanone *O*-oxide **17** Rearrangement of the silanone oxide to the dioxasilirane was not reported.

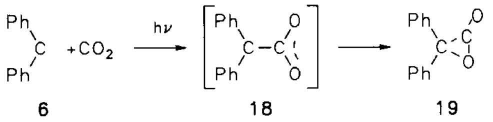


It is not clear if silylenes add O_2 generally in an "end on" fashion (as do carbenes) followed by a rapid cyclization or if the O_2 molecule is added "side on" to produce the dioxasilirane directly. In carbene oxidations the rearrangement of carbonyl *O*-oxides to dioxiranes is only observed photochemically.

As mentioned above, O atoms can be produced in carbene oxidations. The O atoms are highly mobile in solid Ar but can be stored at 10 K as $O(^3P)$ for several hours. The chemiluminescence observed in carbene oxidations is directly related to the production of O atoms (Scheme 3) The extremely exothermic reaction of $O(^3P)$ with a carbene leads to the formation of carbonyl compounds in electronically excited triplet states. Chemiluminescence is observed in both singlet and triplet carbene oxidations; $O(^3P)$ is much less discriminating than $^3O_2$.

DIPHENYLMETHYLENE AND CO_2

Another example of a spin forbidden reaction is the direct carboxylation of triplet carbenes The formation of short lived diradicals (**18**) which rearrange to α-lactones has been proposed [35]. Indirect evidence for the formation of diphenyloxiranone (**19**) during the photolysis of diphenyldiazomethane in the presence of CO_2 has been presented by Wheland and Bartlett [36].



Irradiation of diphenyldiazomethane isolated in Ar matrices doped with up to 10% CO_2 at 543 nm produced carbene **6** in a clean reaction [37]. At these high CO_2 concentrations the carbene is in direct contact with CO_2 but no reaction is observed as long as the matrix is kept at 10 K The absence of reactivity at low temperature indicates that there is a thermal barrier for the spin forbidden reaction. If the matrix is annealed at 35 K, a very slow reaction to yield oxiranone **19** as the sole product is observed. On irradiation into the

T–T absorption of **6** (454 nm) oxiranone **19** is produced rapidly even at 10 K [37]

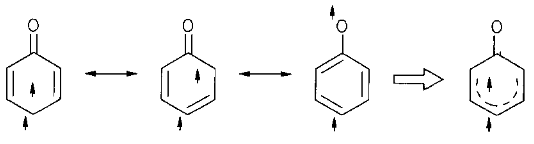
These experiments reveal that there is a thermal barrier for the spin forbidden reaction of CO_2 and **6** in its triplet ground state. The excited triplet state of **6** reacts more like a singlet carbene and readily adds CO_2 to give the α-lactone **19**

4-OXO-2,5-CYCLOHEXADIENYLIDENE

For several carbenes in solution at room temperature the absolute rates of the singlet–triplet interconversions k_{ST} and k_{TS} have been reported [7] Although the S–T interconversion is formally spin forbidden, generally fast ISC is observed For methylene Turro et al [38] reported a rate $k_{ST} \leq 8 \times 10^8 \, s^{-1}$. Aryl substituted carbenes have slightly higher values of 10^9–$10^{10} \, s^{-1}$ [7, 39] Thus to observe the excited singlet state of a triplet (ground state) carbene spectroscopically, picosecond time resolution has to be used.

Due to the different geometry of the S and T states of carbenes k_{ST} should be slowed down in rigid media. Although exact data for k_{ST} as a function of the viscosity of the medium are not available, indirect evidence for the influence of the matrix on k_{ST} has been obtained in the case of diphenylmethylene (**6**) [40]

4-Oxa-2,5-cyclohexadienylidene (**10**) is the first triplet carbene which can be transformed into a metastable singlet species by visible light irradiation in a completely reversible manner [41] Carbene **10** is easily obtained by irradiation of 4-diazo-2,5-cyclohexadienone matrix isolated in Ar at 10 K The triplet ground state was characterized spectroscopically (ESR, IR, UV) as well as chemically (reaction with CO gives a ketene, reaction with O_2 a carbonyl oxide) [28, 41]. According to the ESR spectrum, which shows a comparatively small zero-field parameter D (0.318 cm^{-1}), the mean distance between the unpaired electrons is larger than in most other carbenes The unusually low C–O stretching mode in the IR spectrum (1496 cm^{-1}) also suggests a large contribution of resonance structure **10c** to the wavefunction of **10**



10a 10b 10c 10

Irradiation into the long-wavelength T–T absorption of **10** (543 nm) produces a singlet species (no ESR signal) which has been tentatively assigned as singlet carbene **20** [41] The assignment is based on the following observations:

(i) **20** is only metastable in solid Ar and is converted back to **10** with $t_{\frac{1}{2}} = 165 \pm 30$ h This shows that **20** must be higher in energy than **10** and the barrier for the rearrangement (if there is any) must be considerably smaller than 1 kcal mol^{-1}). A covalent bond is not likely to be broken at these low temperatures.

(ii) A pronounced external heavy atom effect is observed when the reaction rate is measured in Ar, Kr and Xe. This shows that the ISC is the rate determining step.

The S–T rearrangement is not only a thermal reaction but is also induced by IR or visible light irradiation. By using a Nernst glower and a selection of IR band filters as IR source it was possible to show that irradiation into the C–H (or C–D in d_4-**20**) absorption is especially effective in producing **10** [41, 42]. Visible light irradiation into the long wavelength absorption of **20** (λ_{max} = 440 nm) is the most effective way to induce the S–T isomerisation.

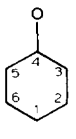
Information about the structure of **10** and **20** was obtained from photooriented [43] species in Ar matrices. Partial conversion of **20** to **10** by irradiation with linearly polarized light at 440 nm produced matrices which exhibited IR dichroism [42]. Both **20** and **10** have been partially oriented in the matrix. Analysis of the data reveals that **10** is planar with C_{2v} symmetry while **20** has lower symmetry. This is consistent with semiempirical MNDO [44] and ab initio calculations (Table 1) [42].

A preliminary interpretation of the Arrhenius plots for the S–T isomerization in Ar and Xe indicates that at temperatures below 20 K the rate k_{ST} is almost temperature independent, whereas at higher temperatures an exponential behaviour is observed. This suggests that there is a thermal barrier for the S–T isomerization which might be overcome at low temperature (below 20 K) by tunnelling.

TABLE 1

Some ground-state properties of **10** and **20** calculated by MNDO

	Triplet[a] **10**	Singlet[b] **20**
C(1)-C(2)[c]	1.390	1.423
C(2)-C(3)[c]	1.408	1.367
C(3)-C(4)[c]	1.494	1.506
C(4)-O[c]	1.239	1.227
C(1)-C(2)-C(3)-C(4)[d]	0	12
νC-O (Experiment)[e]	1496	1713
νC-O (MNDO×0.85)[f]	1599	1782



[a]MNDO-UHF [b]MNDO-RHF [c]Bond length in Å [d]Dihedral angle in degrees [e]Experimental C=O stretching vibration [f]MNDO calculated C=O stretching vibration scaled by 0.85

CONCLUSION

The spin of reactants plays a major role in carbene and silylene chemistry This conclusion can be drawn from room temperature solution experiments as well as from low temperature matrix experiments Formally a spin forbidden reaction can occur via the thermal excitation to excited states of carbenes (for silylenes excited triplet states are too high in energy to play a role in reactions) or intersystem crossing (ISC) must occur along the reaction coordinate. The observation of spin forbidden reactions at low temperature indicates that the conservation of spin is not strict in these reactions and that the spin inversion might well occur during the course of the reaction The observed S–T isomerization of **20** to **10** can serve as a general model for spin forbidden reactions A small barrier for the spin forbidden reaction can be overcome by tunnelling at low temperature If the barrier is very high (as in systems with a large S–T gap) tunnelling is not important (in the time scale of minutes to hours) and no reaction is observed.

ACKNOWLEDGMENT

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