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Carbenes in Matrices—Spectroscopy, Structure, and Reactivity

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Contents

I. Introduction

Ever since matrix isolation spectroscopy was used as an analytical tool, carbenes and related species have been a target of this method. Early reports on reactions of methylene in inert gas matrices were published in 1958[1] and 1959,[2] only a few years after the introduction of this technique by Pimentel et al.[3] and Norman and Porter.[4] Since that time matrix spectroscopy has become a well-established technique in the investigation of reactive species[5–7] and numerous papers on the spectroscopy and reactivity of free carbenes appeared. Various aspects of carbenes in matrices have been recently treated in review articles: triplet carbenes,[8] inert gas matrices,[6,9] and reactive matrices.[10] A related field is time-resolved spectroscopy of singlet[11,12] and triplet carbenes[13–16] in solution at ambient temperature. Review articles of general carbene chemistry and spectroscopy[17] and a new volume of *Houben-Weyl*[18] also contain valuable information on carbenes in matrices. Recently a critical compilation of physical data of carbenes and carbene analogues was published by Nefedov et al., which contains information on IR, UV–vis, ESR, and computational data.[19]

The purpose of this review is to collect information on the chemistry and spectroscopy of matrix-isolated carbenes, with emphasis on isolation in inert-gas matrices such as the noble gases or nitrogen. A prerequisite is that the carbenes were characterized by spectroscopic methods, which in the field of matrix isolation are mainly ESR, IR, UV–vis, or fluorescence spectroscopy. Theoretical methods—especially high level *ab initio* methods—are of increasing importance for the interpretation of spectra. Due to the widespread availability of powerful minicomputers and easy to use quantum chemical programs, calculations will become more widespread in the near future. Thus theoretical results on carbenes have been included in this review as long as they were used for comparison with, or interpretation of, experimental data. Although linear carbon molecules (C_2–C_6) exhibit carbene-like properties (even C_n molecules have triplet ground states while odd C_n molecules are singlets),[20] they are not included in this review.

II. Experimental Methods

A. Matrix Isolation

Matrix isolation is a powerful method for the study of reactive intermediates. The technique was described in several excellent reviews,[7,21–24] and experimental details will not be given here. Three classes of matrices have been used to isolate and study carbenes: (i) inert

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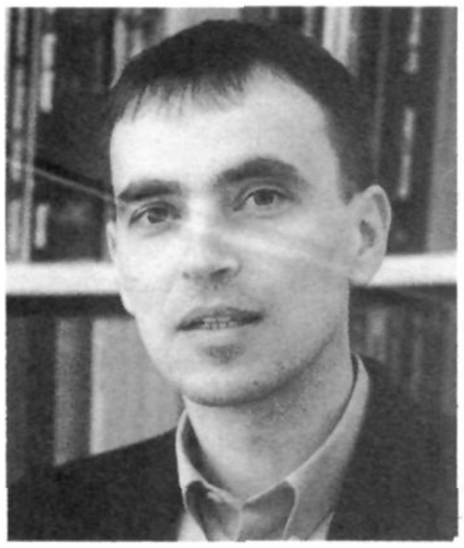


Wolfram Sander was born in Heidelberg, Germany, in 1954. He received his doctoral degree from the University of Heidelberg in 1982 under the guidance of Prof. R. Gleiter and completed his Habilitation in 1989. He was introduced to the matrix isolation technique as a postdoc with Prof. O. L. Chapman at the University of California in Los Angeles (1982–1984). In 1990 he joined the Institute of Organic Chemistry at the University of Braunschweig where he is currently Professor of Chemistry. His research interests include the characterization of reactive intermediates, oxidation reactions with molecular oxygen, and effects of electron spin on chemical reactivity. In 1988 he was awarded the Karl-Freudenberg-Preis of the Heidelberger Akademie der Wissenschaften, and in 1990 he received a Heisenberg-Stipendium and a Winnacker-Stipendium.

Götz Bucher was born in Schwäbisch-Gmünd in 1964 and studied chemistry in Heidelberg and Braunschweig, where he presented a thesis on the matrix photochemistry of oxocyclohexadienylidenes. He is currently doing postdoctoral work with Prof. J. C. Scaiano, University of Ottawa, continuing his studies on transient species with the tools of time-resolved laser spectroscopy.

Stefan Wierlacher was born in Los Angeles, CA, in 1965. He studied chemistry at the Université des Sciences et Techniques du Languedoc at Montpellier, France, and at the University of Heidelberg, Germany, where he received his diploma degree in 1991. Since 1990 he has been working under the supervision of Professor Sander at the Technical University of Braunschweig, where he is currently completing the requirements for his Ph.D. with a predoctoral grant from the Studienstiftung des Deutschen Volkes.

gas matrices, (ii) organic glasses, and (iii) powder matrices. The main differences between these types of matrices are the methods of generating the matrices and the spectroscopic methods which are available for the characterization of trapped species.

(i) Inert gas matrices are produced by codeposition of a noble gas (Ne, Ar, Kr, Xe, where Ar is the most common) or N_2 and a suitable carbene precursor on top of a spectroscopic window placed in a high vacuum system. Carbenes are produced by low temperature (4 K in case of liquid He cooling, around 10 K if closed-cycle He refrigerators are used) photolysis of the matrix-isolated precursors. A requirement for this method is that the precursor can be sublimed without decomposition. By far the most important photolytic precursors are diazo compounds and diazirines. In a few cases carbenes were generated by flash vacuum pyrolysis (FVP) and subsequent trapping of the products with excess inert gas at 10–30 K. Typical matrix ratios (inert gas/carbene precursor) are 500–2000, which prevents largely intermolecular reactions of the carbenes. In most experiments the exact matrix ratio is unknown, and the degree of isolation is guessed from the line width in the IR spectra and from the absence of intermolecular reactions of reactive species. If the carbene precursor is very volatile, matrix ratios can be determined directly by mixing with the matrix gas, otherwise microbalances have been used to determine the rates of deposition of less volatile material.[25,26]

Carbenes are thermally stable in Ar matrices as long as the barrier toward rearrangement is higher than several kilocalories per mole and the temperature is kept below the softening point of the matrix. At tempertures higher than 30–50% of the melting point of the matrix diffusion of trapped species is possible and products of intermolecular reactions are formed.[27]

Reactive matrices are produced similarly by doping the inert matrix gas with a reactive component (e.g. O_2, CO, HCl, CH_3OH) or by codeposition of a reactive matrix gas (e.g. CO_2, ethylene) and carbene precursor on top of a cold window. Reactive matrices allow one to study intermolecular carbene reactions. Reactions of carbenes in O_2- or CO-doped inert gas matrices lead to the formation of characteristic products such as carbonyl *O*-oxides[28] and ketenes[29] and are used to provide chemical evidence for the presence of a carbene.

(ii) Organic glasses are produced by dissolving the carbene precursor in a suitable solvent and cooling below the freezing point.[27] Organic glasses are generally reactive matrices, although reactions of carbenes might be slow at temperatures below 77 K.[10] Perfluorinated solvents are much less reactive than solvents containing H-atoms, but nevertheless can influence the reactivity of carbenes drastically.[30] Their tendency to crystallize—which prevents optical spectroscopy—limits the usefulness of perfluorinated solvents in low-temperature studies. Because of the low infrared transmission of organic glasses in general, IR studies are restricted to small spectroscopic windows, if possible at all. Organic glasses frequently used to characterize carbenes are listed in Table I.

Table I. Abbreviations of Solvents Used in Organic Glasses and Powder Matrices

BZP	benzophenone
DCB	*p*-dichlorobenzene
DMF	dimethylformamide
DPE	1,1-diphenylethylene crystal
EPA	ether/isopentane/ethanol (5:2:5)
Et_2O	diethyl ether
EtOH	ethanol
EtI	ethyl iodide
fluorol	fluorolube glass
HCB	hexachlorobutadiene
HFB	hexafluorobenzene
IP	isopentane
neat	precursor as powder matrix
MCH	methylcyclohexane
MTHF	2-methyltetrahydrofuran
PCTFE	poly(chlorotrifluoroethene)
PFDH	perfluorodimethylhexane
TCB	1,2,3-trichlorobenzene

(iii) Powder matrices are generated by irradiation of the neat precursor—or a solution of the precursor in a solvent which does not produce a glass upon freezing—at low temperatures. The carbene is immersed in the microcrystalline solid which forms the matrix. Secondary reactions such as H-abstractions are observed frequently and due to poor optical transparency (IR as well as UV–vis) the only application possible in this type of matrix is ESR spectroscopy. Due to the high density of carbene molecules available by this method, interactions of the triplet molecules to produce quintet pairs can be studied.[31,32]

B. Spectroscopic Methods

Spectroscopic methods frequently used to characterize carbenes in matrices are (i) IR, (ii) UV–vis, (iii) fluorescence, and (iv) ESR spectroscopy. There are some more special methods, e.g. ENDOR spectroscopy, which will be mentioned in the chapters on individual carbenes.

(i) The absence of intermolecular interactions between trapped species and the absence of rotations (with the exemption of very small molecules such as H_2O or CH_2) of isolated molecules leads to narrow line widths and a high gain of intensity of infrared absorptions.[23,24,33–35] This makes IR spectroscopy—especially FTIR spectroscopy with its additional gain in sensitivity—particularly valuable to characterize matrix-isolated carbenes and other reactive species. Isotopic labeling was used extensively to assign infrared absorptions to specific vibrational modes. Most matrix-IR spectra have been obtained in argon or nitrogen matrices, which are of high optical quality in the infrared region.

(ii) Inert gas matrices as well as organic glasses are suitable for recording UV–vis spectra of carbenes. Compared to IR spectroscopy, lower concentrations are required to obtain UV–vis spectra. In several cases "action spectra" have been measured to assure that the same species is observed with different spectroscopic methods. Triplet carbenes, especially with extended π-systems, exhibit weak to medium intensity absorptions in the visible region of the spectrum, which in many cases show vibrational fine structure. Singlet carbenes generally show intense long wavelength absorptions which are very dependent on substituents. One important aspect of UV–vis spectroscopy is that it provides a link between time-resolved spectroscopy in solution and matrix isolation spectroscopy. UV–vis spectra of the same species obtained by both methods assure that the same chemistry is observed in the solid state and in solution.

(iii) Fluorescence spectra of several carbenes have been obtained in inert gas matrices as well as in organic glasses. Generally the same criteria as for UV–vis spectroscopy are of importance.

(iv) The advantage of ESR spectroscopy is the high selectivity and sensitivity for paramagnetic species such as triplet carbenes, and thus much lower concentrations of carbenes than required for matrix-IR spectroscopy can be easily detected. A large number of carbenes have been characterized by ESR spectroscopy since the pioneering work of Wasserman et al.[36,37] The observation of a stable ESR signal at cryogenic temperatures is generally taken as evidence for the triplet being the ground state of the carbene or at least within a few calories per mole to the ground state. More definite proof comes from the temperature dependence of the ESR signal intensity according to the Curie–Weiss law, but this requires that the carbene be stable to a certain extent at elevated temperatures and no irreversible reactions occur.

The principal information extracted from ESR spectra of triplet molecules in randomly oriented matrices are the zero-field splitting parameters (ZFS parameters) *D* and *E* (interaction energies in cm^{-1}), which measure the magnetic dipole interaction of the unpaired electrons in the absence of an external field.[36,37]

$$D \propto [(r^2 - 3z^2)/r^5] \approx (1/r^3) \tag{1}$$

$$E \propto [(y^2 - x^2)/r^5] \tag{2}$$

D is a measure of the average distance *r* of the unpaired electrons and thus allows the determination of the amount of delocalization in carbenes with conjugated π-systems. *E* measures the difference of the magnetic dipole interaction along the *x* and *y* axes (and thus deviation from cylindrical symmetry) and allows one to estimate the bond angle at the carbene center (especially the *D*/*E* ratio is frequently used to estimate the bond angle).[38] *E* is related to the s character of the in-plane singly occupied orbital. For a linear carbene $E = 0$ is expected (pure p orbital), while decreasing the bond angle leads to a higher s-orbital contribution and a larger value for *E*.

ESR spectroscopy of triplet carbenes was also used to determine the conformation of geometrical flexible carbenes (see individual carbenes).[39] Thus, from the ZFS parameters important information, such as the geometry at the carbene center and the π-electron spin density, can be drawn.

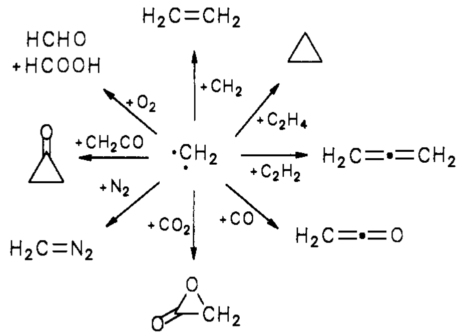
III. Data of Individual Carbenes

A. Acyclic Carbenes without Heteroatoms at the Carbene C-Atom

1. Methylene

Methylene—the parent compound of all carbenes—was investigated in several matrix isolation

Scheme I



studies, the first being reported in 1958 by Milligan and Pimentel[1] and in 1959 by DeMore et al.[2] DeMore et al. photolyzed diazomethane and its deuterated isotopomers $CHDN_2$ and CD_2N_2, matrix isolated (0.35 M) in N_2 at 20 K, and identified ethylene and cyclopropane as the principal products (Scheme I).[2] Although from the IR and UV–vis spectra there was no clear indication of the formation of CH_2, some evidence was provided by chemical trapping experiments. Photolysis of CH_2N_2 in CO-doped N_2 matrices produced ketene, which was easily detected by IR spectroscopy. Trapping of carbenes by CO to produce ketenes is now frequently used to identify matrix-isolated carbenes. The rapid thermal reaction of CH_2 and other carbenes with CO also explains the difficulty in generating carbenes by ketene photolysis in rigid media.

Other intermolecular reactions of CH_2 studied by DeMore et al. are the reaction with ketene to produce cyclopropanone and the reaction with ethylene to produce cyclopropane (Scheme I).[2] In these experiments the—presumably thermal—formation of the final products and photochemical destruction of CH_2N_2 occurs in one step and thus photochemical and thermal reactions are not discriminated.

Milligan and Pimentel[1] first photolyzed (medium-pressure mercury arc lamp) a sample of CH_2N_2 (0.125%) in N_2 at 20 K which produced small amounts of ethylene but no cyclopropane. In the IR spectrum, bands at 1362 and 1114 cm^{-1} appeared which could not be assigned to known compounds. Afterward the matrix was exposed to a "diffusion operation" by warming it to 30–40 K for a short period of time and cooling it back to 20 K. This procedure caused several of the unassigned bands to decrease in intensity, the bands of ethylene to increase, and new bands, assigned to polyethylene, methane, and propene to grow in. This sequence of experiments—irradiation of the matrix at low temperature and subsequent annealing at higher temperature—clearly demonstrates that irradiation of matrix-isolated CH_2N_2 produces reactive species which are trapped in the rigid environment. Warming to 30–40 K permits diffusion of small, matrix-isolated molecules and reactions occur.

Two decades later, Lee and Pimentel reinvestigated the matrix chemistry of methylene.[40,41] The 1362-cm^{-1} band was assigned to methanimine CH_2NH, which is formed during photolysis of CH_2N_2 in inert gas matrices, indicating the high mobility of CH_2. Although CH_2NH also exhibits an absorption at 1114.8 cm^{-1}, evidence was presented that absorptions at 1116 and 819 cm^{-1} are due to the ν_2 bending modes of CH_2 and CD_2, respectively, in the triplet ground state.[40] This value is in good agreement with the 1100–1200-cm^{-1} value obtained in the gas phase from photoelectron detachment studies of CH_2^- [42a] (but see also ref 42b), but considerably higher than the value of 957 ± 10 cm^{-1} obtained by laser magnetic resonance spectroscopy.[42c] Since CH_2 rotates freely in the matrix, the higher value in the matrix might be assigned to a rotation–vibration line.[42c] Recently Russo et al. calculated $\nu_1 = 3039$, $\nu_2 = 962$, $\nu_3 = 3281$ cm^{-1} for triplet CH_2 and $\nu_1 = 2808$, $\nu_2 = 1307$, $\nu_3 = 2909$ cm^{-1} for singlet CH_2 using high level *ab initio* methods, in good accord with the available gas-phase data.[321]

A red thermoluminescence with a maximum at 598.7 nm, which occurred on warming a matrix containing CH_2 above 15 K, was assigned to an emission of electronically excited ethylene (Scheme I).[40] This again demonstrates the high mobility of CH_2 even in low-temperature inert gas matrices.

The extreme reactivity of matrix-isolated CH_2 was shown by trapping experiments with molecular N_2![43] Irradiation of ^{15}N-labeled diazomethane or diazirine in solid N_2 revealed that CH_2 is able to react with a neighboring nitrogen molecule in a matrix cage. These experiments also provided information about the matrix sites occupied by the diazomethane molecule. Maier and Reisenauer came to the same conclusion when investigating the photochemistry of diiodomethane in solid nitrogen.[44] Irradiation at 254 nm produced diazomethane (major product), ethylene, acetylene, and the iodomethyl radical via isodiiodomethane and presumably methylene. Thus, diazomethane and diazirine can only produce methylene in rigid matrices if the nitrogen molecule is able to leave the matrix cage.

An early systematic study of the reactions of CH_2 and simple unsaturated molecules in Ar matrices was conducted by Jacox and Milligan.[45] UV irradiation (cutoff near 220 nm) of CH_2N_2 (1%) and acetylene (1%) in Ar at 4 K produced allene, but no cyclopropene or methylacetylene.[45a] When acetylene-d_2 and CH_2N_2 was used, no scrambling of H and D occurred. A mechanism involving cyclopropylidene as an intermediate was proposed to explain the experimental findings. Irradiation (Pyrex filter) of CH_2N_2 and CD_2N_2 in solid CO_2 at 53 K produced CO, H_2CO (D_2CO), and presumably three further compounds with absorptions between 1894 and 1967 cm^{-1}.[45] Ethylene was only a minor byproduct, which demonstrates that the degree of isolation of CH_2N_2 in CO_2 is comparable to that in Ar or N_2. The absorptions at 1893 and 1900 cm^{-1} were not shifted on deuteration but exhibited red-shifts of 35 cm^{-1} when $^{13}CO_2$ was used in the experiments. Short wavelength UV irradiation caused the intensity of these bands to decrease and CO and CH_2O to build up. On the basis of this evidence the formation of α-lactone as an intermediate in the carboxylation of CH_2 was proposed (Scheme I).

The oxygenation of CH_2 was investigated by Lee and Pimentel.[41] Matrix samples with $CH_2N_2/Ar/O_2$ were irradiated at 8 K and subsequently annealed at higher temperatures. The main products identified by IR spectroscopy were formaldehyde HCHO, formic acid HCOOH, and CO. On warming to 35 K and recooling, absorptions assigned to HCHO and HCOOH slightly increased in intensity. During warming the matrix a chemiluminescence was observed which was attributed

Table II. ESR Data of Methylene and Alkylcarbenes (Chart I)

carbene	matrix[a]	T, K	D/hc, cm^{-1}	E/hc, cm^{-1}	E/D	comments	ref
CH_2	Xe	4.2	0.69	0.003	0.004		47
CH_2	Xe	4	0.6636 0.6881	<0.002 0.00346	<0.003 0.005	two sites with different mobility	46
CHD	Xe	4	0.7443	0.00640	0.0086		49
CD_2	Xe	4	0.7563	0.00443	0.0059		49
	Xe	4.2	0.759	0.0044	0.0058		50
$^{13}CD_2$	Xe	4	0.961	0.0103	0.0107	D–C–D angle 137° (hfs)	51
	Xe	4.2	0.760	0.0043	0.0057	D–C–D angle 137.7°	50
4	MTHF	20	0.689	0.039	0.057	C–C–C angle 143° (E/D ratio)	60
5	neat	14	0.6823	0.038	0.056	C–C–C angle 152° (hfs)	61
6a	PFDH	4	0.712	0.021	0.029	C–C–H angle 160°	63
6b	PFDH	4	0.723	0.027	0.037	C–C–H angle 160°	63
6c	PFDH	4	0.72	0.024	0.033	C–C–H angle 160°	63
7	PFDH	4	0.7444	0.0437	0.059	C–C–H angle 140°	63
8	MTHF	5	0.6860	0.0302	0.044		66a
9	MTHF	5	0.6820	0.0293	0.043		66a

[a] See Table I.

to one or several excited states of HCOOH.[41]

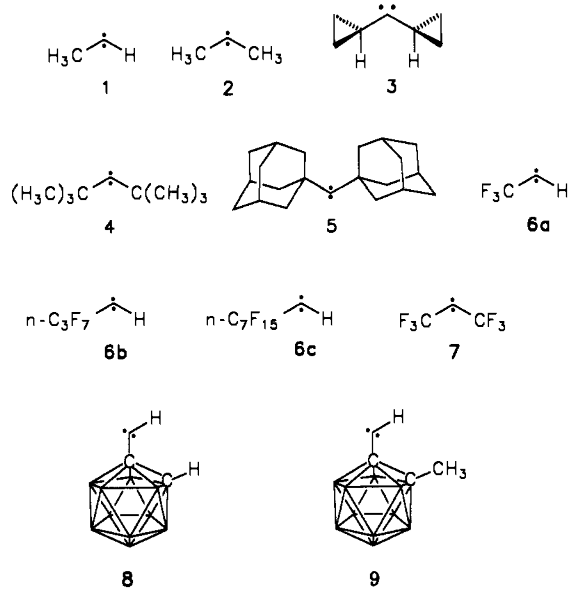
The first ESR studies on methylene appeared in 1970 and demonstrated experimentally that the ground state of CH_2 is a triplet state,[46,47] in accordance with gas-phase investigations[42] and *ab initio* theory.[48] (The most accurate value for the singlet–triplet splitting of CH_2 obtained from far-infrared laser magnetic resonance spectroscopy is 9.05 ± 0.06 kcal/mol.[42d]) Methylene and several of its isotopomers (CHD,[49] CD_2,[49] $^{13}CH_2$,[50,51] and $^{13}CD_2$[50,51]) were generated by irradiation of isotopically labeled diazomethane or diazirine in Xe at 4 K or 77 K (Table II). Both precursors produced the same ESR spectra independent of the temperature, which gives strong evidence for the formation of CH_2. In addition, labeling the carbon nucleus with ^{13}C results in a splitting of the ESR lines to doublets, as expected if only one C-atom is present in the triplet species.[50,51] Three H/D isotopomers (CH_2, CHD, and CD_2) were detected, which proves that two chemically equivalent hydrogen atoms are present. Thus, there is no doubt that CH_2 is indeed the triplet species that was observed in the ESR experiments.

ESR spectra have been particularly valuable in determining the H–C–H bond angle of CH_2. The interpretation of the ESR spectra is complicated by the fact that CH_2 occupies two different sites with different mobility in Xe, which produce two different spectra. Analysis of the zero-field parameters E reveals a bond angle of 136° as the most probable value.[46] Independently, a very similar value was deduced from the hyperfine splitting in $^{13}CD_2$.[50,51]

2. Alkylcarbenes

Due to the low barrier of 1,2-H shifts, most carbenes with α-H atoms are unstable even under the conditions of matrix isolation. *Ab initio* calculations (MP2/6-31G*) predict an activation energy of only 0.9 kcal/mol for the 1,2-H shift in methylcarbene (**1**) but of 6.0 kcal/mol in dimethylcarbene (**2**)[52] (Chart I). The rates of hydrogen shifts might be enhanced by quantum mechanical tunneling (QMT), and therefore the experimental barriers are estimated to be even lower. In an attempt to matrix-isolate methylcarbene (**1**), Seburg and McMahon investigated the photochemistry of diazoethane and methyldiazirine in a variety of inert gas matrices.[53] ESR as well as IR and UV–vis spectroscopic studies failed to provide experimental evidence of **1**. However, in CO-doped matrices methyl ketene was formed, indicating that CO trapping by singlet **1** can compete with hydrogen migration, while ISC to the triplet ground state does not. Modarelli and Platz were able to show in a laser flash photolysis (LFP) experiment, using the pyridine ylide probe method, that deuteration increased the yield of trappable methylcarbene (**1**).[54] The lifetime of singlet methylcarbene-d_4 in pentane at room temperature was estimated to 500 ps and the barrier to its isomerization to less than 2.3 kcal/mol. The same authors presented evidence that dimethylcarbene (**2**) is also a true intermediate with a finite lifetime in solution at room temperature by trapping the carbene with pyridine in an LFP experiment.[55] Thus there is a change that **2** can be trapped in low temperature matrices.

Chart I



The first singlet dialkylcarbene that has been directly characterized in a matrix is dicyclopropylcarbene (**3**).[56] Irradiation (λ = 334 nm) of dicyclopropyldiazirine in N_2 at 6 K produced dicyclopropyldiazomethane and carbene **3** with the strongest IR absorption at 802 cm^{-1} and a broad UV–vis maximum at 490 nm. The observed IR spectrum was in good agreement with the MP2/6-31G(d) calculated spectrum. Subsequent irradiation with λ = 475 nm produced ethylene, cyclopropylacetylene, and 1-cyclopropylcyclobutene. In a CO-doped matrix dicyclopropyl ketene was produced.

Other carbenes bearing α-H atoms which have been trapped in matrices are triplet phenylmethylcarbene (phenylethylidene) (**56**),[57] phenylcarbenes **58–62** and **64** (Chart IV), and the singlet carbenes cyclopropylchlorocarbene (**201**),[58] benzylchlorocarbene (**202**)[59] (Chart XIV), and methoxymethylcarbene (**211**) (Chart XV).

Several alkylcarbenes without α-H atoms were generated and spectroscopically characterized in matrices. Di-*tert*-butylcarbene (**4**) is sufficiently stable to be observed in MTHF glass at 20 K by ESR spectroscopy (Table II).[60] At temperatures above 70 K the carbene disappeared irreversibly. From the E/D ratio a bond angle at the carbene center of 143° was estimated,[60] which might be a lower limit.[61] Irradiation of neat di-*tert*-butyldiazomethane at 14 K and subsequent warming to room temperature gave mainly products typical of a singlet carbene.[60]

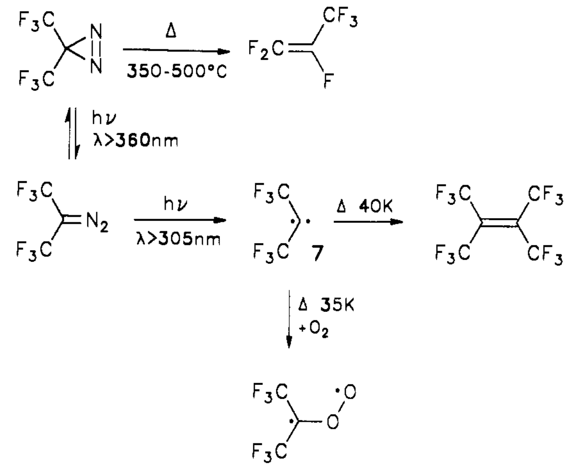
Unlike **4**, diadamantylcarbene (**5**) shows substantial triplet reactivity.[61,62] Irradiation of diadamantyldiazomethane labeled with ^{13}C at the central position produced carbene [^{13}C]-**5** (Table II). The Curie law was obeyed, and from the hyperfine splitting a bond angle of 152° was estimated. The wide angle enforced by steric interactions stabilizes the triplet state of **5** compared to the singlet.[61]

In contrast to the simple alkylcarbenes, fluorinated alkylcarbenes are thermally more stable and have been characterized in several low-temperature studies. Wasserman et al.[63] demonstrated that (trifluoromethyl)carbene (**6a**), (heptafluoropropyl)carbene (**6b**), (pentadecafluoroheptyl)carbene (**6c**), and bis(trifluoromethyl)carbene (**7**)—produced by irradiation of the corresponding diazo compounds in perfluorodimethylhexane at 4 K—have triplet ground states (Table II). From the ESR data, bond angles at the carbene centers were estimated to 160° (**6a–c**) and 140° (**7**), which reveals that an additional CF_3 group reduces the angle at the carbene center. In the same study during warmup of solutions containing both **7** and O_2 a strong chemiluminescence was noted, which was identical to the phosphorescence of hexafluoroacetone.[63]

Irradiation of bis(trifluoromethyl)diazirine[64] or bis(trifluoromethyl)diazomethane[65] in Ar at 12 K produced **7**, and its IR spectrum was recorded (Scheme II). FVP (0.001 Torr, 350–500 °C) of the diazirine gave only hexafluoropropene and no carbene, indicating a rapid 1,2-shift of fluorine atoms at high temperatures.[64] Warming of matrix-isolated **7** to 40–45 K caused the IR bands assigned to the carbene to disappear and bands of the carbene dimer to grow in. In the presence of CO (Ar/CO = 5/1) bis(trifluoromethyl) ketene was formed.[64]

The reaction of **7** with $^3O_2$ in O_2-doped Ar matrices has also been reported.[65] Annealing a 1% O_2-doped Ar matrix containing **7** for several minutes at 35–40 K leads to the complete disappearance of the carbene and formation of hexafluoroacetone *O*-oxide (Scheme II). The O–O stretching mode of the carbonyl oxide is found at 997 cm^{-1} and red-shifted by 35 cm^{-1} in the $^{18}O_2$-labeled compound. The carbonyl oxide is very photolabile, and irradiation with $\lambda > 590$ nm produced hexafluoroacetone as the principal product. The rapid formation of a carbonyl oxide in a thermal reaction at low temperature provides further evidence for the carbene being produced on irradiation of the diazo precursor and suggests a triplet ground state for **7**,[65] in accordance with ESR studies.[63] In contrast to the clean thermal oxygenation of the carbene, the in-cage photooxidation of the diazo precursor leads to a variety of products such as CO_2 and COF_2, which shows that C–F bonds are cleaved under these conditions.

Scheme II



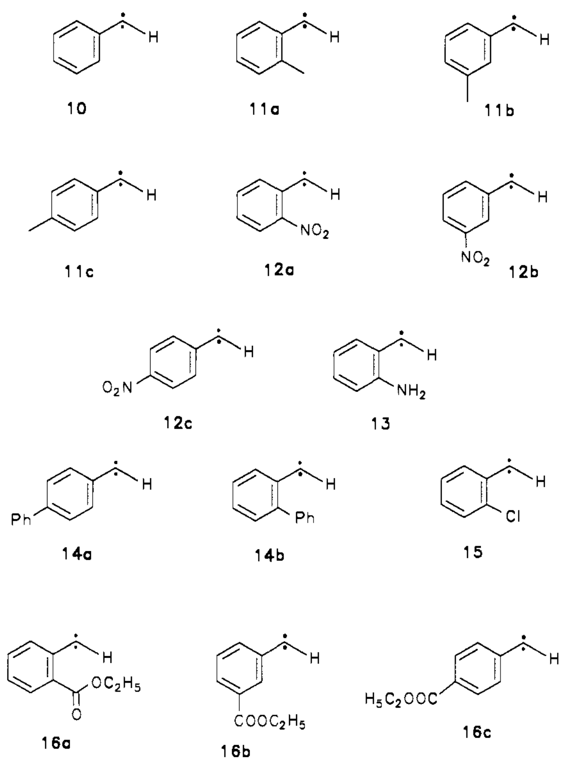
During annealing the matrix a chemiluminescence was observed,[65] in accordance with the earlier observation of Wasserman et al.[63] in organic glasses. The chemiluminescence starts at very low temperature (warming the matrix from 10 to 15 K) and was identified as phosphorescence of hexafluoroacetone. From these experiments it was concluded that the chemiluminescent step is the combination of carbene **7** and triplet oxygen atoms leading to triplet hexafluoroacetone.[65]

Hutton and Roth reported ESR data of the two *o*-carboranylcarbenes **8** and **9** in MTHF at 5 K (Table II).[66a] The observation of a triplet ESR spectrum was taken as evidence for the triplet being the ground state or lying within a few calories of the ground state. A π-spin density of 0.9 at the carbene center—corresponding to a largely localized π-system—was estimated from the large value of the ZFS parameter D. In contrast to the linear boron-substituted 3-*o*-carboranylcarbenes **215** and **216**, a substantial E value was observed for **8** and **9** (Table II), indicating a bent carbene structure. From *ab initio* calculations on several model carboranylcarbenes McKee concluded that (i) the singlet–triplet splitting is small in these carbenes, (ii) insertion into the C–H bond of adjacent CH_3 groups is accompanied with a substantial activation barrier, and (iii) the fused cyclopropenyl ring/cage system is more stable than the carbene.[66b] The stability of **8** and **9** might be associated with the extra stability of a closo 12-vertex cage compared to the expanded 13-vertex cage.

3. Phenylcarbene

Phenylcarbene (**10**, Chart II) is a triplet ground state carbene, which has been characterized in the course of a number of spectroscopic studies employing matrix isolation in noble gases, organic glasses, single crystals, or polycrystalline samples. The most common precursor for **10** is phenyldiazomethane, but the sodium

Chart II



salt of benzaldehyde tosylhydrazone[67a] and diazidophenylmethane[67b] were also successfully used for its generation.

The ESR spectrum of **10** was reported early in the 1960s by Trozzolo, Wasserman, Murray, and Yager.[68,69] Zero-field splitting parameters $D = 0.518\ \text{cm}^{-1}$ and $E = 0.024\ \text{cm}^{-1}$ are indicative of spin delocalization within the phenyl ring (albeit less than in diphenylcarbene) and show that **10** cannot be a linear molecule. Confirmation of this conclusion was obtained from an investigation of ^{13}C-hyperfine splitting, using 1-^{13}C labeled phenyldiazomethane.[69] More recently, the fluorescence spectrum of **10** in 3-methylpentane matrix at 77 K was measured by Haider et al.[70] in a laser-induced fluorescence (LIF) study. This technique had to be applied as phenylcarbene is stable in organic matrices only on a time scale of minutes. Emission maxima were found at 445 and 476 nm. Prior to this observation, the formation of **10** from 2,3-diphenyloxirane had been postulated by Becker et al.[71] The emission spectrum (λ_{max} = 389 and 414 nm) reported by these authors, however, fits neither the LIF spectrum of Haider, nor is it consistent with the absorption spectrum measured by Chapman (see below); thus there is severe doubt whether Becker's assignment of **10** is correct. A way to circumvent the difficulties imposed by the high reactivity of phenylcarbene is to utilize noble gas or nitrogen matrices; it was done first in 1982 by Chapman et al.,[72] who were able to record the infrared and UV–vis absorption spectra of **10**. The latter spectrum exhibits a long-wavelength band system with a rich fine structure and a prominent maximum at 430 nm, while the IR spectrum of **10** offers much less characteristic features. Phenylcarbene is unstable toward visible light irradiation ($\lambda > 416$ nm); it rearranges to yield cyclohepta-1,2,4,6-tetraene. The reaction is apparently not straightforward, and it will be discussed in some detail later. Subsequent studies on **10** in Ar matrix dealt with its reaction with triplet oxygen.[73,74]

All three isomeric tolyldiazomethanes yield benzocyclobutene and styrene on thermolysis. This intriguing result prompted a number of investigations,[75] utilizing ^{13}C-isotopic labeling, or matrix isolation spectroscopy. In the course of such a matrix study, Chapman et al.[76] were able to observe the three tolylcarbenes by UV–vis, IR, and ESR spectroscopy. The least stable member of the family proved to be *o*-tolylcarbene (**11a**), which undergoes a very facile thermal hydrogen shift to yield *o*-xylylene,[57] but *m*- and *p*-tolylcarbene (**11b** and **11c**) also rearrange upon irradiation (see section IV.A). The spectroscopic properties of the three tolylcarbenes are very similar, all of them exhibiting a richly structured absorption extending in the visible region from about 395 to 450 nm. The IR spectra do not show any particularly characteristic absorptions, and from the ESR spectra zero-field splitting parameters around $D = 0.51\ \text{cm}^{-1}$ and $E = 0.024$–$0.025\ \text{cm}^{-1}$ can be derived (Table III). Further phenylcarbene derivatives that have been characterized include (3- and 4-nitrophenyl)carbene (**12b**[77] and **12c**[77]), as well as 4- and 2-biphenylylcarbene (**14a**[77] and **14b**[78]), and (2-chlorophenyl)carbene (**15**), which was characterized in Ar matrix by IR and UV spectroscopy.[79] **12b,c** and **14a,b** were observed by means of ESR spectroscopy; as expected, relative to **10** the *D* value decreases in **12c** and **14a** due to extended π-delocalization, but surprisingly it is higher in **12b**!

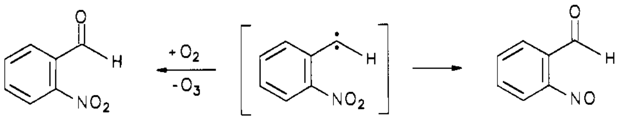
Ortho-substituted carbenes such as **11a** are in many cases subject to atom transfer from the ortho substituent to the carbene center and thus labile even under the conditions of matrix isolation. (2-Nitrophenyl)carbene (**12a**) and (2-aminophenyl)carbene (**13**) are two examples of this class of carbenes.[80] Irradiation ($\lambda > 350$

Table III. Spectroscopic Properties of Phenylcarbene Derivatives (Chart II)

carbene	matrix[a]	*T*, K	D/hc, cm^{-1}	E/hc, cm^{-1}	E/D	absorption λ, nm	emission λ, nm	ref(s)
10	DCB	77	0.5150	0.0251	0.04873			69
	fluorol	77	0.518	0.024	0.046			68
	Ar	10				430	455, 476	72, 70
11a	Ar	10–15	0.503	0.0253	0.05030	413–450		76
11b	Ar	10–15	0.517	0.0246	0.04758	394–448		76
11c	Ar	10–15	0.516	0.0240	0.04651	395–444		76
12b	*b*		0.5230	0.0243	0.04646			77
12c	*b*		0.4859	0.0224	0.04610			77
14a	*b*		0.4788	0.0277	0.05785			77
14b	Et_2O	77	0.510	0.020	0.03922			78
15	Ar	10				456, 308		79

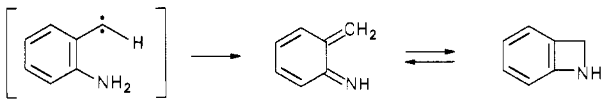
[a] See Table I. [b] Not specified.

nm) of (2-nitrophenyl)diazomethane matrix-isolated in argon at 10 K provided 2-nitrosobenzaldehyde by intramolecular oxygen migration.[80a] Carbene **12a** could be trapped as 2-nitrobenzaldehyde in 20% oxygen-doped argon matrices, but direct spectroscopic characterization of the carbene was not possible.



12a

Similarly, photolysis (λ = 544 n, argon, 11 K) of (2-aminophenyl)diazomethane produced 6-methylene-2,4-cyclohexadien-1-imine, which on shorter wavelength photolysis was converted to benzazetine.[80b]



13

The chemistry of the three isomeric (carbomethoxyphenyl)carbenes **16** was subject of a communication by Tomioka et al.[81a] The ortho isomer **16a** could not be isolated, but reacted intramolecularly with the carbonyl function to yield an ylide. **16b** and **16c** could be obtained, but spectroscopic data were not given. Finally, the radical cation derived from phenylcarbene was observed and published by Miyazaki et al.[81b] [γ-Irradiation of phenyldiazomethane in *n*-butyl chloride at 77 K yields its radical cation (λ_{max} = 515 nm), which is destroyed upon irradiation, forming $10^{\bullet+}$ (λ_{max} = 475 nm)].

4. Diphenylcarbene

The chemistry of diphenylcarbene **17** has been extensively investigated in Ar matrix as well as in Shpolskii matrices. Additionally, a number of studies were published utilizing benzophenone (BZP) or 1,1-diphenylethylene (DPE) single crystals as ordered matrices. The literature includes numerous product studies, UV–vis (Table IV), ESR (Table V), ENDOR, and IR spectroscopic studies; an overwhelming amount of information has been gathered, and much of this work has already been reviewed.[19,77,82–84] The wealth of knowledge may be due to the fact that with diphenyldiazomethane a precursor is available which is prepared and handled in a relatively simple way and which yields the carbene under very mild photolytic conditions. **17** has also been generated photolytically from triphenyl-[71,85] and tetraphenyloxirane,[71,86,87] from 2,2,4,4-tetraphenyloxetan-3-one,[86,87] from the sodium salt of benzophenone tosylhydrazone,[67a,88] and from diazido-[67b] and dichlorodiphenylmethane [in the presence of tetrakis(dimethylamino)ethylene].[89] For most of the carbene studies it is also a benefit that **17** (Chart III), unlike phenylcarbene, does offer the advantage of photostability under short wavelength photolytic conditions.

Among arylcarbenes, diphenylcarbene was the first to be characterized spectroscopically. Attempts to obtain spectral information started in the late 1950s, and research activities have not come to an end today.

a. ESR Spectroscopy. The first ESR spectroscopic data for **17** were presented in 1962 by Murray, Trozzolo, Wasserman, Cramer, and Yager,[68,90,91] and, practically at the same time, by Brandon, Closs, and Hutchison (Table V).[92] In these studies Wasserman et al. utilized fluorolube glass as matrix, whereas Closs et al. measured the ESR spectrum of **17** in a benzophenone single crystal at 77 K. This work confirmed Skell's prediction[93] that **17** should be a triplet ground state molecule. Closs et al. found ZFS parameters of D = 0.4050 cm^{-1} and E = 0.0186 cm^{-1}, which showed for the first time that considerable spin delocalization occurs within the molecule and that there is a significant deviation from the predicted linear D_{2d} symmetry.[93] Another important finding from Wasserman's studies[68] was the observation of a bright blue chemiluminescence upon warming of **17** in O_2-doped glasses which was attributed to benzophenone phosphorescence (this was later confirmed by us[74]). Using 1-^{13}C-enriched samples, both Closs[92] and Wasserman[69] could also measure the ^{13}C-hyperfine splitting; but proton hyperfine splitting was not observed. The ESR spectrum of **17** as a function of the matrix material was examined by Trozzolo, Wasserman, and Yager.[94] Brandon et al. studied the ESR spectrum of **17** in a benzophenone single crystal in greater detail.[95] More recently, a study of **17** in BZP was published by Sixl et al.,[96] who found a change in the ESR spectrum upon warming the crystal up to 60 K, which is caused by release of the N_2 molecules. **17** is assumed to reside substitutionally into benzophenone crystals, so that the individual **17** molecules are well aligned (one has to pay attention, however, to the fact that benzophenone undergoes a phase transition on cooling from 77 to 2 K[97]). Consequently, the fine structure tensors shows a large anisotropy with respect to the orientation of the external magnetic field. One can make further use of this alignment in electron-nuclear double resonance (ENDOR) experiments; in the case of **17**, this was done first by Hutchison and Kohler.[98] ENDOR studies on **17** were also published by Doetschman and Hutchison (in 1,1-diphenylethylene at 77 K),[99] as well as by Anderson and Kohler (in benzophenone at 2 K).[100] The results can be summarized as follows: **17** is a bent molecule with C_2 symmetry (in DPE;[99] in BZP at 2 K only C_1 symmetry is observed;[100] in this case the two benzene rings have slightly different angles to the C8–C1–C2 plane). The C8–C1–C2 bond angle is 140.0°,[100] (ref 78,[99] 148°) and the phenyl substituents are rotated out of the C8–C1–C2 plane by 36° [99] (ref 79[100] gives 29.9° and 26.2°). The spin density at C1 was calculated to be 0.620; positive spin density is also found at the ortho and para positions.[100] This is already a quite detailed picture of the reactive species diphenylcarbene!

Another approach to obtain aligned samples of **17** is to irradiate the diazo precursor (*a priori* without orientation, in an organic glass) with plane polarized light. According to Dunkin et al.,[101] this leads to a well-observable polarization of the ESR spectrum, and it also allows the determination of the orientation of the transition moment leading to photofragmentation of the diazo compound within the molecular framework: the diazo compound must have absorbed the light along the CNN axis.

Table IV. UV–Vis Spectroscopic Data of Diphenylcarbenes (Chart III)

carbene	matrix[a]	T, K	λ, nm absorption[b]	 excitation[c]	 emission[d]	$t_{1/2}$, ns	ref
17	MTHF	77	300,465		480		112
	BZP	4.2	448,485				116
	BZP	4.2	471.18[e]				116
	MCH	77			483[e]	121	122
	BZP	10				320–360	120
	BZP	25				140	119
	MCH	77				108	117
	EtOH	77				87	117
	EtOH/EtI	77				72	117
d_{10}-17	BZP	4.2	463.5				116
	BZP	4.2	469.55[e]				116
18	MTHF	77	301,472		487		112
	MTHF	77	311,472		487		121
	MCH	77			486[e]		122
19	MTHF	77		335–345	495		112
	MTHF	77	322,480		495		121
	MCH	77[f]	324,458	320,420,478	489	77.1	118
	EtOH	77[f]	320,380,460	328,410,480	495	79.4	118
	EtOH/EtI	77[f]	323,422,475	323,422,475	492	74.5	118
20	MTHF	77		335–345	507		112
	MCH	77[f]	330,485	330,485	504	66.8	118
	EtOH	77[f]	330	328		72.1	118
	DMF	77[f]				59	118
21	MTHF	77	311,475		487	110	112
	MTHF	77	317,475		487		121
	BZP	4.2	482.57[e]				116
	MCH	77			492[e]		122
22	MCH	77			500[e]		122
23	MTHF	77	316,475		488		112
	MTHF	77	319.5,477		488	91	121
	BZP	4.2	483.91[e]				116
	MCH	77			491[e]	32	122
24	MCH	77[f]	270,328,480	270,326	498	11.4	118
	EtOH	77[f]	270,325,480	268,324	499	11.4	118
	EtOH/EtI	77[f]	483	284,327,483	497	11.7	118
25	MTHF	77	265,370,555				112
26	MCH	77[f]	325,390				118
	EtOH	77[f]	295,365,565				118
27	MTHF	77		355	555		112
	MCH	77			557[e]		122
28	MTHF	77	332,496		510		121
	MCH	77[f]	320,480	325,460,475	510	84.0	118
	EtOH	77[f]	330,460,495	330,460,495	510	74.6	118
	EtOH/EtI	77[f]	330,460,495	330,458,495	511	66.4	118
	MCH	77			510[e]	88	122
29	MCH	77[f]	332,470,510	332,425,510	526	69.5	118
	EtOH	77[f]	334,475,510	333,475,512	530	65.9	118
	EtOH/EtI	77[f]	336,473,512	336,475,510	530	59.5	118
39	MCH	77			492[e]	109	122
40	MCH	77			482[e]	830	122
41	MCH	77			486[e]	1600	122
42	MCH	77			516[e]		122

[a] See Table I. [b] Absorption maxima. [c] Absorption maxima derived from excitation spectra. [d] Emission maxima. [e] 0–0 transition. [f] Variable-temperature study 4–95 K, data in table obtained at 77 K.

Several studies dealt with the influence of para substituents on the ESR spectrum of diphenylcarbene (Table V). All of the DPC derivatives investigated so far proved to be triplet ground state molecules, as was shown by means of a Curie plot in many cases. Humphreys and Arnold examined a series of 4-substituted and 4,4′-disubstituted DPC derivatives, laying particular stress on the investigation of 4-donor-4′-acceptor substituted systems.[88,102,103] As a general trend, para substitution of the DPC molecule results in a decrease of the D parameter, which is proportional to $1/r^3$, r being the average separation of the unpaired electrons. This effect, which is obviously due to extended π-delocalization of spin density, is never very large; the most prominent deviation from the D value of 17 is observed in donor–acceptor-substituted molecules like 34.[88] Humphreys and Arnold explained this observation in terms of merostabilization, i.e. participation of charge-separated mesomeric structures with favorable energy (cf. Katritzky et al.[104]). It is evident that electronic factors exert significant influence on carbene structure, but steric hindrance imposed by bulky ortho substituents may equally alter its properties, the best examined example being dimesitylcarbene (41). Its ESR spectrum, which was reported by Nazran, Griller, and co-workers,[105–107] shows zero-field splitting parameters of $D = 0.3460\ \mathrm{cm^{-1}}$ and $E = 0.0082\ \mathrm{cm^{-1}}$, which are significantly lower than in other diphenylcarbene derivatives. Probably in 41 the aryl groups are close to perpendicular, as dimesityldiazo-

Table V. ESR Data of Diphenylcarbenes (Chart III)

carbene	matrix[a]	T, K	D/hc, cm^{-1}	E/hc, cm^{-1}	E/D	ref
17	BZP	77	0.4055	0.0194	0.0478	69
	BZP	77	0.4050	0.0186	0.0459	92
	BZP	77	0.40505	0.01918	0.0474	95
	DPE	4	0.39644	0.01516	0.0382	98
	BZP	80[b]	0.406	0.019	0.0468	96
	BZP	2	0.407783	0.020625	0.0506	97
	fluorol	77	0.401	0.0186	0.0464	68
	MCH	77	0.4053	0.0190	0.0469	85
	MCH/IP	5	0.4088	0.0170	0.0416	102
18	*c*	*c*	0.4071	0.0188	0.0462	77
19	MCH/IP	5	0.4043	0.0191	0.0472	102
	MTHF	10	0.406	0.0193	0.0475	108
	neat	10	0.408	0.0180	0.0441	108
20	MCH/IP	5	0.4022	0.0189	0.0470	102
	MTHF	10	0.407	0.0198	0.0486	108
	neat	10	0.408	0.0197	0.0483	108
21	*c*	*c*	0.4029	0.0194	0.0482	77
22	MTHF	10	0.399	0.0194	0.0486	108
	neat	10	0.398	0.0194	0.0487	108
23	*c*	*c*	0.3921	0.0191	0.0487	77
25	neat	77[d]	0.3778	0.0173	0.0458	88
26	THF	77[d]	0.3773	0.0177	0.0469	88
28	MCH/IP	5	0.3906	0.0180	0.0461	102
	MCH/IP	77[d]	0.3906	0.0193	0.0494	88
29	MCH/IP	77[d]	0.3879	0.0178	0.0459	88
30	MCH/IP	77[d]	0.3774	0.0172	0.0456	88
31	neat	77[d]	0.3518	0.0163	0.0463	88
32	THF	77[d]	0.3696	0.0171	0.0463	88
33	THF	77[d]	0.3611	0.0172	0.0476	88
34	THF	4[e]	0.3551	0.0164	0.0462	88
35	THF	77[d]	0.3994	0.0178	0.0446	88
36	THF	77[d]	0.3876	0.0168	0.0433	88
37	MTHF	77[d]	0.3748	0.0180	0.0480	88
38	neat	10	(triplet)			109
41	IP/Et_2O	5.8	0.3460	0.0082	0.0237	105
41[f]	IP/Et_2O	5.8	0.3558	0.0125	0.0351	105

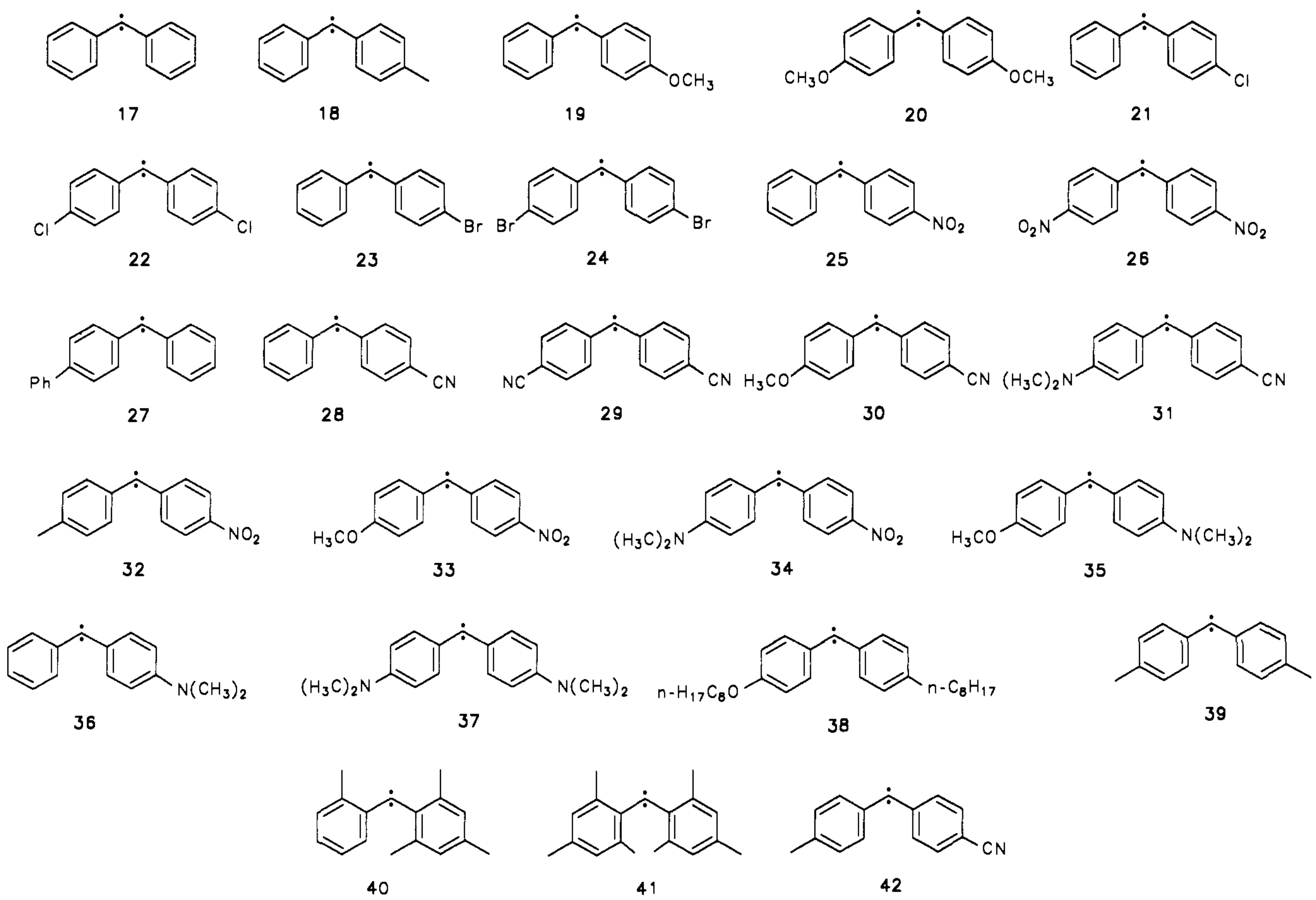
[a] See Table I. [b] Irreversible change at 106 K. [c] Not specified. [d] Variable-temperature study 4–30 K, ZFS parameters at 77 K. [e] Signal not strong enough at higher temperature. [f] Before annealing (measured at 6 K).

methane was shown by X-ray crystallography[106] to exhibit a dihedral angle between the aryl groups of 90°, which can be expected to be similar in the carbene. Another interesting observation was made by Nazran and Griller when they compared the ESR spectra of **41** before and after annealing the sample from 6 to 77 K; the shifts in the ZFS parameters are consistent with an expansion of the central C–C–C angle upon thermal relaxation of the matrix.

Iwamura et al. photolyzed polycrystalline solid samples of the diazo precursors of **19**, **20**, and **22**.[108] Apart from the corresponding triplet carbenes they could also detect quintet ground state carbene pairs of **19** (D = 0.136 cm^{-1}; E = 0.013 cm^{-1}) and **20**, but not of **22**. The quintet carbene pair behaves magnetically like a separate molecule and is stable up to 60 K. The crucial difference between **19** and **20** on one side and **22** on the other side is found in the way the phenyl rings stagger in the corresponding diazo crystals; pseudopara orientation of the phenylmethylene substituents was observed in the diazo compounds yielding **19** and **20**, whereas pseudogeminal orientation was found in the case of **22**. This is exactly analogous to the situation in the case of the bis(phenylmethylene)[2.2]paracyclophanes (see section III.A6). Ferromagnetic interaction between carbene molecules was observed by Iwamura et al. also in the case of **38**.[109] All these examples of organic ferromagnetism are in accord with McConnell's prediction that higher spin states should be observed where the individual paramagnetic molecules are staggered in a way that positive spin density in one molecule comes close to negative spin density in its neighbor.[110]

b. UV–Vis Spectroscopy. In 1959, DeMore, Pritchard, and Davidson published the first study intended to gain evidence for the existence of **17** in a matrix at 20 or 77 K;[2] however, they could observe only products of secondary carbene reactions, i.e. benzophenone and benzophenone azine (in fact, the reported absorption band at 465 nm may well have been due to **17**). The emission, absorption, and excitation spectra of **17** (in 2-methyltetrahydrofuran glass) were first recorded by Gibbons and Trozzolo (Table IV).[111,112] They could locate the emission maximum at 480 nm; the corresponding absorption spectrum shows a λ_{max} at 465 nm and could additionally be derived from an excitation spectrum. The assignment to **17** was based on a correlation of the measured fluorescence intensity with the intensity of the ESR signal of **17**. Gibbons and Trozzolo were able to record data for several 4-substituted diphenylcarbene derivatives (Table IV). The visible absorption of **17** was also reported independently by Moritani et al.[113] Closs, Hutchison, and Kohler could obtain the optical absorption spectrum of **17** in a DPE single crystal.[114] Utilizing linearly polarized light, they demonstrated that the transition moment of the absorption leading to photofragmentation of the diazo compound should lie along the line of the phenyl ring centers (this is in contradiction to ref 80[101]). The absorption and emission spectra of **17** in benzophenone crystals at extremely low temperatures were recorded by Anderson et al.,[115] by Graham and Lin (high-resolution absorption spectra of **17**, d_{10}-**17**, **21**, and **23**),[116] and by Sixl et al. (Table IV).[96] Measuring at 4.2 and 2 K, Anderson, Kohler, and Stevenson[115] could detect a distinct fine structure, corresponding to a zero-phonon line (470.7 nm) and its phonon sidebands. Due to large excitation–phonon coupling, the fine structure features were practically not observable at 30 K. The fluorescence lifetime and quantum yield of diphenylcarbene were recorded by Sullivan and Ware,[117] and in an extensive study, which also included absorption, excitation, and emission spectra of a series of its derivatives, by Ono and Ware.[118] The fluorescence lifetime of **17** was determined to be 123 ns in methylcyclohexane glass at 77 K, it is only slightly shortened to 73 ns by admixing ethyl iodide. 4-Substitution in all cases also led to a shortened emission lifetime, the most prominent example being the dibrominated compound **24** with $t_{1/2}$ = 11.4 ns (in MCH). Further detailed investigations on the fluorescence of **17** were performed by Graham and Wohler (in BZP crystal, sensitized luminescence of **17**),[119] by Graham and Wang (influence of a magnetic field on BZP sensitized luminescence of **17**),[120] and by Fujiwara et al.,[121] who compared the fluorescence maxima of diphenylcarbenes in solution at room temperature (RT), measured by laser flash photolysis (LFP), with the fluorescence maxima in low-temperature organic glasses. In the case of **17**, the emission in the matrix is blue-shifted by 25 nm relative to solution phase which the authors explain in terms of matrix effects on the geometry of the carbene triplet excited state. Similar effects were found by Scaiano and Weir

Chart III



(Table IV).[122] As in the case of phenylcarbene, the radical cation of **17** has also been characterized. Miyazaki et al.[81b] irradiated diphenyldiazomethane in an *n*-butyl chloride matrix at 77 K with γ-rays and could observe the radical cation of the diazo compound (λ_{max} = 650 nm), which upon irradiation yields $\mathbf{17}^{\bullet+}$ (λ_{max} = 390 nm). ESR signals of the species were detected as well.

c. *Infrared Spectroscopy.* Compared to the amount of publications dealing with ESR and absorption and emission spectra of diphenylcarbene, studies employing infrared spectroscopy in noble gas or nitrogen matrices are relatively scarce. The infrared spectrum of **17** was first observed by Hess[123] in 1984; more recently, an extensive investigation including carbon-13 isotopic labeling has given a more complete picture about the vibrational spectrum of **17** and also allowed assignment of some of the bands.[74,124] The C8–C1–C2 asymmetric stretching fundamental can be assigned to a very weak band at 1282 cm^{-1} (^{13}C-shift −24 cm^{-1}), other bands exhibit only small isotopic shifts and are mainly due to vibrations of the two phenyl ring moieties.[74]

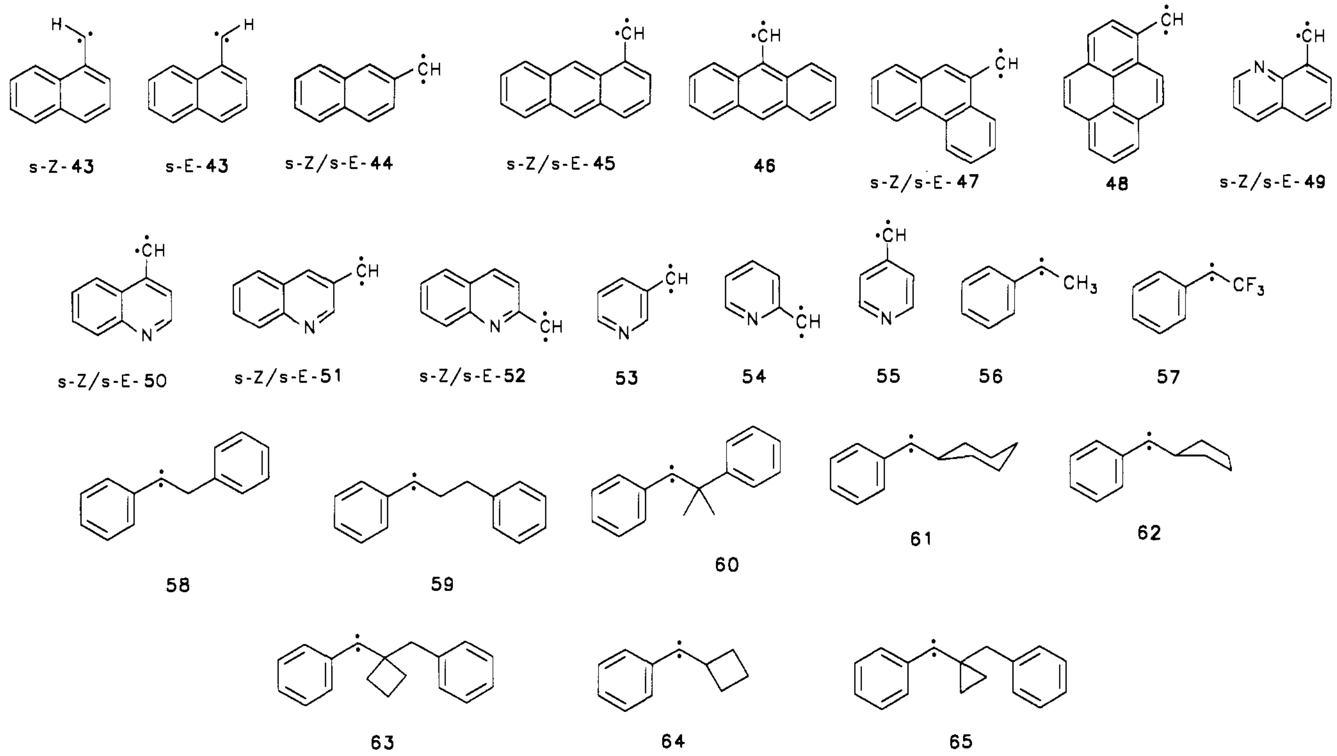
5. Other Acyclic Arylcarbenes

As in the case of many other carbenes, the first ESR spectrometric characterization of 1- and 2-naphthylcarbene (**43** and **44**, respectively, Chart IV) stems from the laboratory of Trozzolo and Wasserman.[125]

It is particularly interesting that in both cases a mixture of two rotational isomers, namely *s-Z* (or *syn*) and *S-E* (or *anti*), was found. The isomers could be readily distinguished by ESR spectroscopy (Table VI); an assignment of the two triplet signals to the stereoisomers was possible. (This was confirmed later by calculations performed by Hutton and Roth.[126]) As expected, the *D* values are lower than in phenylcarbene. A subsequent kinetic analysis by Senthilnathan and Platz[127] revealed that *s-E*-**43** is probably lower in energy than the *s-Z* isomer; and at the same time it is more reactive. The two observations only seem to be contradictive, they are readily explained in terms of steric interaction. Chapman et al.[128a] attempted to obtain optical and infrared absorption spectra of **43** and **44**, but due to the lower sensitivity of absorption spectroscopy (compared to ESR spectroscopy) they were only able to observe products derived from a carbene–cyclopropene rearrangement. This work was recently continued by Albrecht and McMahon, who were able to characterize 2-naphthylcarbene (**44**) by IR, UV–vis, and ESR spectroscopy.[128b] Photolysis (λ = 560 nm) of carbene **44** produced 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene, which in turn on shorter wavelength irradiation (λ = 290 nm) exclusively ring opened to **44**. Ring expansion to a cycloheptatetraene or rearrangement to 1-naphthylcarbene (**43**) was not observed.

Spectroscopic evidence for the emission spectrum of **44** was delivered by Haider, Platz, Despres, and Migirdicyan;[70] emission bands were observed at 569, 575, and 598 nm. If the 8-position in the naphthalene moiety of **43** is substituted by a methyl group, the carbene can no longer be observed; even at liquid helium temperature and even in the case of the deuterated

Chart IV



isotopomer, quantitative rearrangement (via a tunneling mechanism) to triplet 1,8-naphthoquinodimethane does occur.[129–133] It has to be noted that this extreme case of instability toward hydrogen shift is restricted to the carbene case; the corresponding nitrene was characterized via its ESR spectrum.[134]

Among the monoarylcarbenes which have not been discussed thus far, 1-[39] and 9-anthrylcarbene[125] (**45** and **46**, respectively), 9-phenanthrylcarbene (**47**),[39] and 1-pyrenylcarbene (**48**)[127] proved to be less elusive. In the case of **45** and **47** (but not in **48**), where geometrical isomerism of the carbenes is to be expected, Roth and Hutton[39] could in fact determine the *D* values of the two isomers; they could also correlate the experimental results with calculations. An attempt to generate 4-phenanthrylcarbene remained unsuccessful.[39] Further work by the same group dealt with a series of quinolylcarbenes,[135] which are closely related to the naphthylcarbenes and which exhibit similar properties: Geometrical isomerism is observed, and spin density can be delocalized more efficiently when the carbene moiety is in 4- or 8-position (**49** and **50**, respectively).

The series of pyridylcarbenes constitutes a group of heteroaromatic carbenes showing great similarity to the phenylcarbene family. It was investigated by Chapman and co-workers, utilizing IR[136] and ESR[137] spectroscopy. Geometrical isomerism, although in principle to be expected in **53** and **54**, was not observed. Chemical evidence for the formation of carbene **53** was provided by the formation of 3-pyridyl ketene in CO-doped Ar matrices. Irradiation ($\lambda > 360$ nm, Ar, 10 K) of both **53** and **55** produced the same azacycloheptatetraene (**183**).[136]

In a way similar to dialkylcarbenes, most arylalkylcarbenes bearing α-H atoms undergo very rapid intramolecular hydrogen shift in their singlet states to form styrene derivatives. Thus they might seem to be rather elusive species, but obviously at cryogenic temperatures ISC is sufficiently effective in these molecules to allow the detection of their triplet ground states in matrices. The first example of this group to be discussed here, phenylmethylcarbene (phenylethylidene) (**56**), was first detected by Murray.[77] Some years later, Chapman, McMahon, and West[76] could obtain **56** in an Ar or Xe matrix and characterized it via ESR and IR spectroscopy. The observation, that the isomerization of **56** requires temperatures of 65 K in Xe matrix, indicates a considerable barrier to hydrogen shift imposed by spin restrictions. Due to the high dissociation energy of the C–F bond, phenyl(trifluoromethyl)carbene **57** does not need such protection. It was characterized as a ground-state triplet molecule by means of ESR spectroscopy by Wasserman et al.[63] and by IR spectroscopy by Mal'tsev and coworkers.[138] A series of further arylalkylcarbenes, including, for example, the interesting phenylcyclopropylcarbene **65**, was described in publications by Platz et al.[139] and by Trozzolo and Wasserman.[77] Platz and co-workers could not observe the parent phenylcyclopropylcarbene (ring expansion to phenylcyclobutene did occur quantitatively), but they were able to detect the benzyl-substituted derivative **65**. Its ESR spectrum, and to a lesser degree those of the cyclobutyl derivatives, indicate some spin delocalization into the cyclopropane (cyclobutane) ring (relatively small *D* value).

A number of diarylcarbenes remain to be reviewed in this section.

1- and 2-naphthylphenylcarbene (**66** and **67**, Chart V) were examined in three studies by Fujiwara et al.,[140] by Maloney and Platz,[141] and by Migirdicyan, Platz, and co-workers.[142] The Japanese group was able to characterize both **66** and **67** by ESR spectroscopy, by optical absorption, and by laser-induced fluorescence.

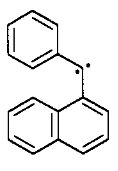
Table VI. ESR Data of Arylcarbenes (Charts IV and V)

carbene	matrix[a]	T, K	D/hc, cm^{-1}	E/hc, cm^{-1}	E/D	comments	ref
43	BZP	4,77	0.4347	0.0208	0.0478	*s*·*Z*	125
	MCH	6	0.4425	0.0221	0.0499	*s*-*Z*	135
	BZP	4,77	0.4555	0.0202	0.0443	*s*-*E*	125
	MCH	6	0.4629	0.0201	0.0434	*s*·*E*	135
44	BZP	4,77	0.4926	0.0209	0.0424	*s*-*Z*	125
			0.4711	0.0243	0.0516	*s*-*E*	
	Ar	10	0.500	0.0242	0.0484	*s*·*Z*	128b
			0.480	0.0277	0.0577	*s*-*E*	
45	*b*	*b*	0.390	*b*		*s*·*Z*	39
			0.420	*b*		*s*·*E*	
46	BZP	4,77	0.3008	0.0132	0.0439		125
47	*b*		0.436	*b*		*s*·*Z*	39
			0.470	*b*		*s*-*E*	
48	*i*·PrOH	77	0.40	0.019	0.0475		127
49	MCH	6	0.4434	0.0225	0.0507	*s*-*Z*	135
			0.4641	0.0225	0.0485	*s*·*E*	
50	MCH	6	0.4666	0.0219	0.0469	*s*-*Z*	135
			0.4865	0.0207	0.0425	*s*·*E*	
51	MCH	6	0.4975	0.0202	0.0406	*s*-*Z*	135
			0.4702	0.0245	0.0521	*s*-*E*	
52	pcarb[c]	6	0.5313	0.0246	0.0463	*s*-*Z*	135
			0.5038	0.0251	0.0498	*s*·*E*	
53	Ar	12	0.513	0.0241	0.0470		137
54	Ar	12	0.537	0.027	0.0503		137
55	Ar	12	0.533	0.0248	0.0465		137
56	Ar	10–15	0.508	0.0278	0.0547		76
	b		0.4957	0.0265	0.0535		77
57	neat	4	0.5183	0.0313	0.0604		63
58	*b*		0.493	0.0289	0.0588		77
59	MTHF	10	0.502	0.027	0.0538		139
60	MTHF	10	0.498	0.026	0.0522		139
71	MTHF	10	0.492	0.025	0.0508		139
62	MTHF	10	0.500	0.028	0.0560		139
63	MTHF	10	0.488	0.026	0.0533		139
64	MTHF	10	0.488	0.026	0.0533		139
65	MTHF	10	0.473	0.026	0.0550		139
66[d]	MTHF	77	0.353	0.016	0.0453		140
67[d]	MTHF	77	0.384	0.020	0.0521		140
67	MTHF	77	0.3898	0.0195	0.0500	*s*·*Z*	141
			0.4044	0.0168	0.0415	*s*·*E*	
68[e]	MTHF	15	0.3157	0.0109	0.0345		143
68[f]	MTHF	15	0.2609	0.0051	0.0195		143
69	DAK[g]	4–480	0.113	0.0011	0.0097		144
70	MTHF	11–50[h]	0.3720	0.0161	0.0433		166
71	MTHF	11–50[h]	0.3730	0.0156	0.0418		166
72	MTHF	11–50[h]	0.3837	0.0168	0.0438		166

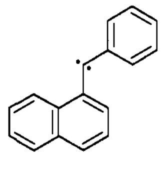
[a] See Table I. [b] Not specified. [c] Propylene carbonate. [d] The values represent the average of the two rotameric forms. [e] before annealing, Curie law obeyed at 15–50 K. [f] After annealing at 80 K. [g] 9,9′-Dianthryl ketone, measured at 4 K (the values represent upper limits). [h] Variable-temperature study.

The measurements in the UV–vis range unveiled a long wavelength absorption ranging up to 600 nm and a corresponding emission in the region 575–700 nm, with maxima at 598 (**66**) and 584 nm (**67**). The emission is quite short-lived in both cases (10 and 17 ns in **66** and **67**, respectively). The ESR spectra obtained by Fujiwara et al. point to a high degree of spin delocalization within the aromatic system. Geometrical isomerism is to be expected in both compounds, but the Japanese authors did not try to further resolve the spectra, which was then done for **67** by Maloney and Platz.[141] In a subsequent joint effort of Platz's team in Ohio with Migirdicyan's group in Paris, temperature, magnetic field, and concentration effects on the fluorescence behavior of **66** and **67** were examined in considerable detail.[142] One of the interesting results: The emission spectra of both carbenes are dictated to a large extent by the naphthalene moiety. For example, the vibrational fine structure in the fluorescence spectrum of **67** can be analyzed very conveniently in terms of the normal modes of the naphthalene molecule. The emission

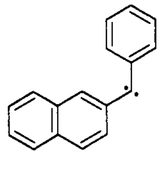
Chart V



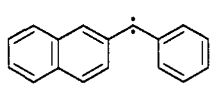
s-Z-66



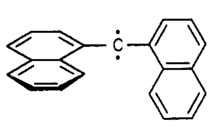
s-E-66



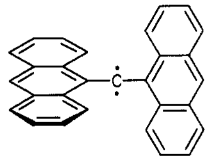
s-Z-67



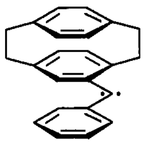
s-E-67



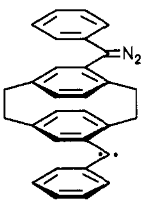
68



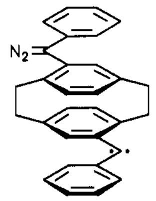
69



70



71



72

spectra of both carbenes consist of broad and sharp bands, the relative intensity of which depend critically on sample concentration, temperature, and irradiation duration; i.e., on sample history. Di-1-naphthylcarbene (**68**) was subject of work published by Tukada, Iwamura, and coworkers.[143] Its ESR spectrum, measured at 15 K, is very typical for a bent carbene molecule with extensive spin delocalization. Upon annealing, however, geometrical relaxation takes place (a similar effect was reported by Griller et al. in the case of dimesitylcarbene), and the carbene assumes a linear structure, as shown by the ZFS parameters. This change is irreversible, recooling does not build up the first signal again.

9,9′-Dianthrylcarbene (**69**) is a sterically highly hindered molecule which exhibits many unusual properties. Its chemistry was examined by ESR spectroscopy by Wasserman et al.[144] and by optical absorption spectroscopy in matrix as well as by a number of time-resolved techniques in solution by Griller and coworkers.[145] In solution, it reacts with $^3O_2$ nearly 5 orders of magnitude slower than all other triplet carbenes, and the main mode of decay is self-quenching, which is diffusion controlled, in spite of the bulky molecular framework. In an anthracene matrix, it can be detected at temperatures as high as 160 °C! The reason for all this exotic behavior is found in its linear geometry and, therefore, in the fact that the spin density is nearly completely delocalized within the molecule. The ZFS parameters given in Table VI were measured at 4 K and represent the upper limits; at higher temperatures,

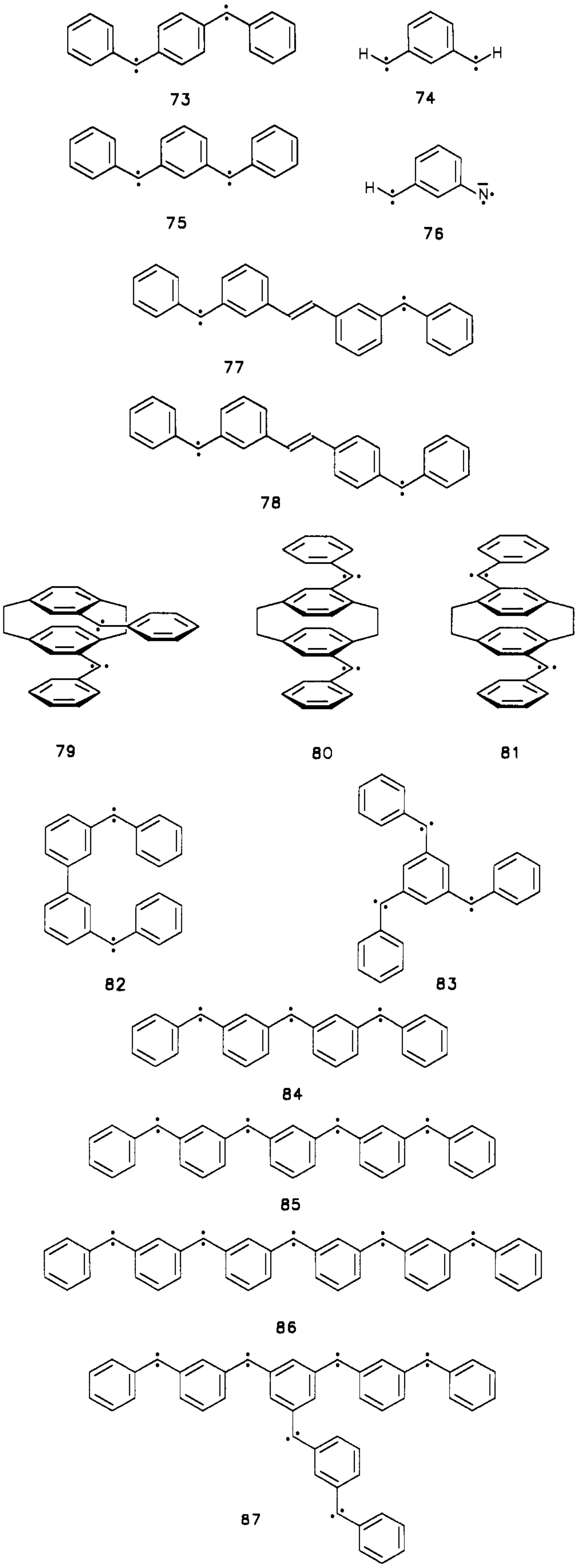
E is virtually zero.[144] Finally, the UV spectrum of **69**, matrix-isolated in isopentane/ether, shows two maxima at 355 and 445 nm.[145]

6. Di-, Oligo-, and Polyarylcarbenes

One of the topics of current interest in carbene research is the generation of molecules with a large number of carbene "functional groups". The aim is to achieve ground-state spin multiplicities as high as possible and thus to approach organic para- and ferromagnetism. Because of possible technical applications this field is of high interest and has been reviewed several times.[19,77,82,146–148] The first dicarbene reported in the literature dates from 1963, when the generation of *p*-phenylene bis(phenylcarbene) (**73**, Chart VI) was published by Trozzolo et al.[149] It turned out to be a nearly linear ground-state triplet molecule with extensive spin delocalization, which is best described in terms of a *p*-benzoquinodimethane diyl type structure (Table VII). A later study, performed by Sixl et al.,[96] yielded a somewhat more complicated picture of the chemistry of **73** and its diazo precursor, including a highly labile monodiazo–monocarbene intermediate, which splits off the second molecule N_2 thermally with a very low activation energy.

During the last two decades, research activities on di- and oligocarbenes have focused on compounds with *m*-phenylene-bridged carbene centers, as this class of carbenes is promising for the generation of organic high-spin molecules. Applying Longuet-Higgins' theory,[150] in 1963 Trozzolo et al. calculated that *m*-phenylene biscarbenes **74** and **75** should have quintet ground states;[149] the ZFS parameters were published two years later by Wasserman et al.[151] and, independently, by Itoh (Table VII).[152] A closely related compound is the mixed carbene–nitrene derivative, (3-nitrenophenyl)-carbene (**76**), which was reported by Tukada, Mutai, and Iwamura.[153] It also has a quintet ground state; the D value lies almost exactly between those of **74** and *m*-phenylenedinitrene.[151] A more exotic species, the radical anion of **75**, may also be mentioned at this place; it was generated by successive γ-irradiation and visible irradiation of the diazo compound, and it proved to have a doublet ground state (the quartet excited state is very easily accessible).[154]

Chart VI



The concept of linking carbene centers by *m*-phenylene bridges was further extended by Japanese researchers; subsequently, septet,[155,156] nonet,[156–160] undecet,[161] and very recently the world-record tridecet[162] spin multiplicity could be achieved. Two different types of carbene arrangements were utilized: One-dimensional chains as in **84–86**, and two-dimensional networks as in 87 and, in its elementary form, **83**. The most thoroughly examined example of this group of high-spin molecules is the nonet tetracarbene **85**, which was investigated in a series of elaborate studies by the group centered around Iwamura. The system was surveyed by means of ESR spectroscopy (Table VII)[157,158] and by measuring the paramagnetic susceptibility;[159,160] the results show that it exhibits a number of quite interesting features, among them conformational changes upon annealing (as indicated by the ESR spectra), a single-photon photodissociation of the tetradiazo compound to the tetracarbene, the onset of antiferromagnetic intermolecular interactions below 65 K when measured in MTHF glass, and a large saturation effect on the magnetization of **85**, if a strong external magnetic field is applied at low temperatures (Table VII). By comparing the magnetic behavior of **85** with that of

Table VII. ESR Data of Di- and Oligocarbenes (Chart VI)

carbene	matrix[a]	T, K	multiplicity[b]	D/hc, cm^{-1}	E/hc, cm^{-1}	E/D	ref
73	DBB[c]	77	T	0.0521	<0.002	<0.03839	149
	BZP	180	T	0.065	0.005	0.07692	96
74	*d*		Q	0.0844	0.0233	0.2761	151
75	*d*		Q	0.0701	0.020	0.2853	151
	BZP	77	Q	0.07131	0.01902	0.2667	152
75	MTHF	3.1–77	D[e]				154
	MTHF	3.1–77	quartet[e,f]	0.1200	0.0045	0.0375	154
76	MTHF	18	Q	0.124	0.002	0.0161	153
77	MTHF	16–65	S				163
	MTHF	16–65	Q[f]				163
78	MTHF	16–65	Q				163
79	MTHF	11	Q	0.0624	0.0190	0.3045	166
	MTHF	11	T[f]	0.1872	0.0570	0.3098	166
80	MTHF	11	S				166
	MTHF	11	T[f]	0.1840	0.0023	0.0125	166
81	MTHF	11	Q	0.1215	0.0085	0.06996	166
82	BZP	4.2	S				165
	BZP	4.2	T[f,h,i]	0.29583	0.06032	0.2039	165
	BZP	4.2	Q[f,h,i]	0.10349	0.01457	0.1408	165
	BZP	4.2	T[f,i,k]	0.23895	0.06452	0.2700	165
	BZP	4.2	Q[f,i,k]	0.08329	0.02114	0.2538	165
83	DBB[g]	4.2	septet	0.04158	0.01026	0.2468	155
84	BZP	77	septet	0.06670	0.00045	0.00675	156
85	BZP	1.8–56	nonetet	0.03161	0.00394	0.1246	158
86	TBB[l]	77	undecet	0.0168	0.0036	0.2143	161
87	MTHF	10	tridecet				162

[a] See Table I. [b] Ground-state multiplicity (if not stated otherwise); S, singlet; D, doublet; T, triplet; Q, quintet. [c] 1,4-Dibenzoylbenzene. [d] Not specified. [e] Radical anion. [f] Excited-state multiplicity. [g] 1,3-Dibenzoylbenzene. [h] Low-temperature form. [i] The singlet, triplet, and quintet states are nearly degenerate. [k] High-temperature form. [l] 1,3,5-Tribenzoylbenzene.

comparable metal particles with less than 30-Å diameter, the authors came to the conclusion that **85** does not behave like a molecular ferromagnet, but rather like a molecular superparamagnet.[160] Similar properties have been found recently in the case of the tridecet hexacarbene **87**.[162]

The game of connecting carbene subunits to complicated oligomeric structures has also been played with linking units other than *m*- or *p*-phenylene bridges. Examples are ethylene-bridged compounds such as **77** and **78** and the 3,3′-biphenyl-bridged molecule **82**. **77** and **78** were described by Murata, Sugawara, and Iwamura;[163] the meta,meta′ isomer **77**, which has to be labeled "disjoint" according to the theory of Borden and Davidson[164] has a singlet ground state, the quintet (and probably also the triplet) state is thermally accessible at 50 K. The meta,para′ isomer **78** ("nondisjoint"), on the other hand, is expected to have a quintet ground state, which is confirmed by the experiment. Compound **82** was examined by Itoh.[165] In this case, the singlet (which is the ground state), triplet, and quintet states are almost degenerate; the most significant effect of temperature on the ESR spectra is observed at 140 K, when an irreversible change in conformation takes place.

A completely different approach to induce paramagnetic interaction between carbene molecules can be achieved by stacking the phenyl rings of the carbene units in such a way that positive spin density in one molecule comes close to negative spin density in its neighbor, according to McConnel's relationship,[110] which is observed for example in partially irradiated crystals of some diphenyldiazomethane derivatives.[108,109] (See section III.A.4.) A more systematic exploration of this type of carbene interaction was published by Izuoka et al.,[166] who incorporated two carbene units into a [2.2]paracyclophane skeleton, so that both phenyl rings were connected to only one divalent carbon atom. The resulting relative orientations of the carbene centers are labeled pseudo ortho as in **79** and pseudometa or pseudopara as in **80** or **81**, respectively (Table VII). As expected according to theory, **79** and **81** show paramagnetic behavior with quintet ground states (a triplet state is thermally accessible in **79**), whereas in **80** the two diphenylcarbene subsystems interact in an antiferromagnetic fashion (again, a triplet excited state may be populated thermally). As byproducts, monodiazomonocarbenes were also characterized by ESR spectroscopy (Table VI). The spin densities in **79**–**81** were subject of a recent theoretical study by Sinha and Ramasesha.[167]

7. Vinyl- and Ethynylcarbenes

The vinylcarbene–cyclopropene rearrangement is of considerable interest in preparative organic chemistry[168] and therefore this reaction has been studied in some detail.[169–172]

Photolysis of vinyldiazomethane in a variety of organic glasses at 6 K produced vinylcarbene (**88**, Chart VII) in its triplet ground state.[39,173] Two distinct ESR spectra were recorded and assigned to a pair of geometric isomers with the hydrogen at the carbene center in *s*-*Z* and *s*-*E* position (Table VIII). The assignment is based on a simple point spin model,[126] from which a lower *D* value for the *s*-*E* rotamer is calculated. In the range 6–15 K the Curie law is obeyed, as it is required for triplet ground-state species.

The *s*-*Z*/*s*-*E* ratio varies between 0.65 and 0.05, depending on the matrix, temperature, and irradiation time. From the *E*/*D* ratio the H–C–C bond angle at the carbene center is estimated to 140°.[173]

The spin density on C-1 was estimated by comparison of the average *D* value of *s*-*E* and (*s*-*Z*)-vinylcarbene

Chart VII

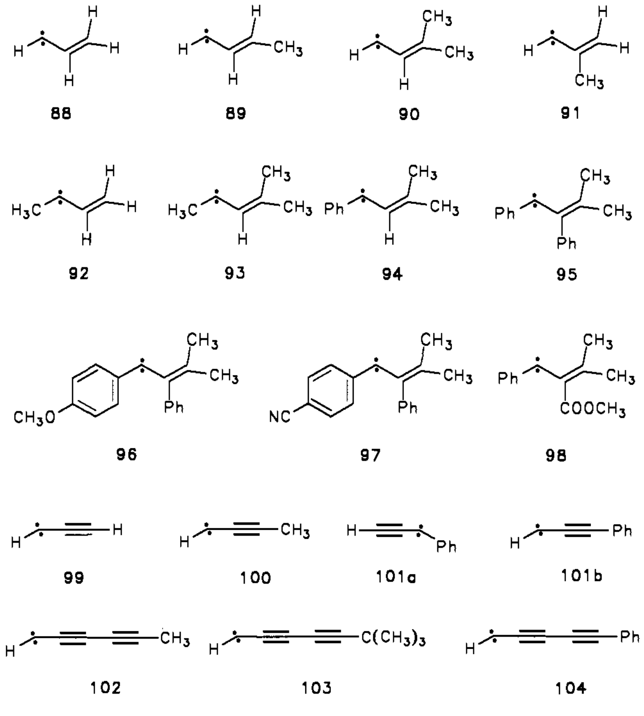
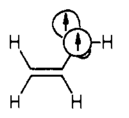


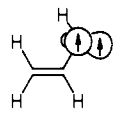
Table VIII. ESR Data of Vinyl- and Ethynylcarbenes (Chart VII)

carbene	matrix[a]	T, K	D/hc, cm^{-1}	E/hc, cm^{-1}	E/D	comments	ref
88	MTHF	6	0.4093	0.0224	0.0547	*s-E*	173
			0.4578	0.0193	0.0422	*s-Z*	
89	neat	*b*	0.4078	0.0233	0.0571	*s-E*	39
			0.4574	0.0208	0.0455	*s-Z*	
90	neat	*b*	0.4124	0.0237	0.0575	*s-E*	39
			0.4538	0.0202	0.0445	*s-Z*	
91	neat	*b*	0.4009	0.0249	0.0621	*s-E*	39
			0.4310	0.0249	0.0578	*s-Z*	
92	neat	*b*	0.3990	0.0220	0.0551	*s-E*	39
			0.4531	0.0200	0.0441	*s-Z*	
93	neat	*b*	0.4002	0.0220	0.0550	*s-E*	39
			0.4421	0.0234	0.0529	*s-Z*	
94	neat	*b*	0.357	0.0194	0.0543	*s-Z*	39
95	MCH/IP (4:1)	5	0.3580	0.0206	0.0575		175
96	MCH/IP (4:1)	5	0.3336	0.0179	0.0537		176
97	MCH/IP (4:1)	5	0.3368	0.0182	0.0540		176
98	MCH/IP (4:1)	5	0.3643	0.0166	0.0456		175
99	PCTFE	77	0.6276	0.0	0.0		177
100	PCTFE	77	0.6263	0.0	0.0		177
101	PCTFE	77	0.5413	0.0035	0.00647		177
102	PCTFE	77	0.6087	0.0	0.0		177
103	PCTFE	77	0.6055	0.0	0.0		177
104	PCTFE	77	0.5530	0.0	0.0		177

[a] See Table I. [b] Not specified.



s-E



s-Z

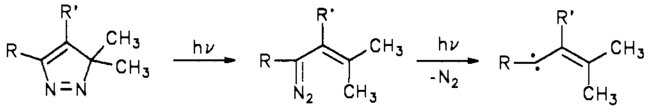
with that of CH_2 (Table VIII) to 0.58.[39,173] Thus the delocalization of the unpaired electron in the π-system is similar to that of the allyl radical, while the second unpaired electron is localized in a σ-orbital at C-1.

Both rotamers are stable below 15 K but rapidly react to form products of unknown constitution at 77 K.[173] At temperatures between 20 and 35 K, 88 decays with $E_a < 200$ cal/mol, the *s-E* isomer decays somewhat faster than the *s-Z* isomer. At temperatures far below the melting point of the matrix, diffusion processes are expected to be very slow, and thus intramolecular rather than intermolecular processes—presumably via ISC to the singlet surface—are responsible for the decay of 88. A likely intramolecular reaction is ring closure to cyclopropene.

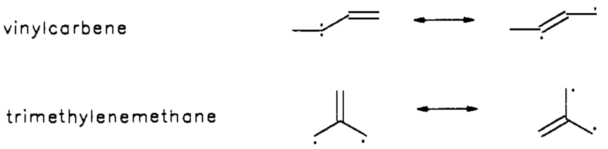
Methyl-substituted vinylcarbenes **89**–**93**, generated by irradiation of substituted diazopropenes in frozen solution, exhibit the same type of geometric isomerism as **88**, while for **94**, with a phenyl group at the carbene center, only one isomer was observed.[39]

Chapman described the selective formation of the *s-E* and *s-Z* conformers of 88, characterized by IR and ESR spectroscopy, by irradiation of the corresponding rotamers of diazopropene in inert gas matrices.[174] UV irradiation (λ > 340 nm) produced cyclopropene, allene, and methylacetylene as the major products.

Arnold et al. generated a series of vinylcarbenes **95**–**98** with aryl substituents at the carbene center by irradiation of 3*H*-pyrazoles or vinyldiazomethanes in organic glasses at 5 K (Table VIII).[175,176] The vinyldiazomethanes were synthesized by irradiation of 3*H*-pyrazoles in solution at 10 °C and are stable at room temperature for several hours. The stereochemistry of the pyrazoles or vinyldiazomethanes is presumably preserved upon irradiation, which rationalizes that only the *s-E* rotamers of vinylcarbenes **95**–**98** were detected.



Curie law dependence was observed between 5 and 45 K, which proves the triplet ground state of these carbenes. The *D* values correspond to a mean separation of the unpaired electrons of approximately 2 Å, indicating a higher degree of localization than in trimethylenemethanes.



Irradiation of the cyclopropene corresponding to **95** did not produce the carbene or other triplet species,[175] which was explained by the low rate of ISC in the cyclopropenes and by the observation that triplet cyclopropenes do not ring open in other systems.[176]

Bernheim et al.[177] generated propargylene **99** and several of its derivatives **100**–**104** by irradiation of the corresponding ethynyl diazo compounds with the Pyrex-filtered light of a mercury arc lamp in poly(chlorotrifluoroethylene) at 77 K. Characterization of the carbenes by ESR spectroscopy allowed the authors to draw some conclusions about the electronic structure of propargylenes. For all derivatives—except phenylpropargylene (**101**)—an *E* value of zero was determined. The explanation of this was that **99** and its derivatives are linear (but see discussion below), and thus the π-system can be interpreted as a superposition of two linear allyl radical π-electron structures. In **101** the delocalization of spin density is expanded over the phenyl π-system, and therefore a measurable value for *E* is observed. The delocalization is also reflected in a lower D value—a consequence of the larger mean distance of the unpaired electrons—for the phenyl-substituted derivatives compared to the parent carbene **99**.

Infrared spectra of propargylene and partially deuterated isotopomers were reported by Chi and Leroi,[178] who prepared the carbenes by irradiation ($\lambda > 350$ nm) of diazopropyne, matrix isolated in krypton at 30 K. IR absorptions at 3285, 2140, 408, and 259 cm^{-1} were assigned to fundamental vibrations of **99**. Only one C–H stretching frequency was observed, which implies that both H-atoms are equivalent, and thus a linear structure was deduced from the IR data. Some evidence for the formation of **99** by vacuum ultraviolet photolysis of propyne in Ar at 14 K was given by Jacox and Milligan.[179]

Maier et al. generated **99**, d_1-**99**, and d_2-**99** by photolysis of diazopropyne as well as cyclopropenylidene in Ar at 12 K.[180,181] Fundamental vibrations were now assigned to absorptions at 3265.5 (s), 1620.0 (vw), 550.4 (m), 401.6 (m), and 245.9 (s) cm^{-1}, in agreement with high-level *ab initio* calculations. (The 2140-cm^{-1} absorption described by Chi and Leroi[178] is obviously due to a contamination, the isomeric vinylidenecarbene (**192**) exhibits the antisymmetric C═C═C vibration around 1950 cm^{-1}.) The calculations also show that propargylene is a nonrigid molecule, and the anharmonicity of the potential surface has to be taken into account to reproduce IR frequencies and especially intensities. The nonrigidity is caused by a very low lying transition state (0.09 kcal/mol according to MP4/6-311++G(df,pd) calculations by DeFrees and McLean[182]) which separates the two degenerate bent structures. Thus the matrix IR data provide experimental evidence for the calculated structures.

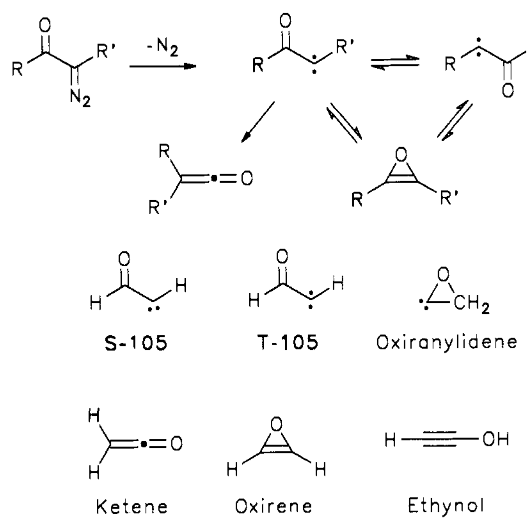
Propargylene **99** was formed in a photostationary equilibrium with vinylidenecarbene **192** and cyclopropenylidene **132** (Scheme VIII).[180,181] Irradiation at 313 nm produces high yields of vinylidenecarbene (**192**) and small amounts of cyclopropenylidene (**132**), and at 254-nm irradiation **192** again rearranges to **99**.

IR, UV–vis, and ESR spectra of phenylpropargylene (**101**) were recently reported by DePinto and McMahon.[183] Photolysis of 1-phenyldiazopropyne in Ar at 10 K produced 1-phenylpropynylidene (**101a**) as the only major photoproduct. Warming the matrix to 37 K resulted in the disappearance of **101a** and in the formation of its isomeric 3-phenylpropynylidene (**101b**). The spectra were assigned by using ^{13}C-labeling, and from the ESR hyperfine splittings bond angles at the carbene carbon atoms of 158–160° and 157–158° were calculated for **101a** and **101b**, respectively.

B. α-Carbonylcarbenes

α-Carbonylcarbenes are of considerable interest as intermediates in the Wolff rearrangement.[19] There has been some discussion whether singlet ketocarbenes are energy minima on the hypersurface, or loss of nitrogen in the diazo precursor and rearrangement are concerted reactions. As a result of *ab initio* calculations Nguyen et al. propose that during the retro-Wolff-type rearrangement of a diazafulvenone to cyanovinyl isocyanate the singlet ketocarbene is not a distinct intermediate.[185] The isolation of triplet ketocarbenes in low-temperture matrices, however, suggests that at least in some cases the singlets are long lived enough at low temperature for ISC to occur (Scheme III). The alternative route to triplet ketocarbenes is ISC of excited diazo precursors with subsequent spin-allowed cleavage to produce the triplet carbenes.

Scheme III



Another point of interest is the oxirene system, which is a potential intermediate in the ketocarbene–ketene rearrangement. Matrix isolation spectroscopy is the method of choice to shed some light on these rather complcated processes.

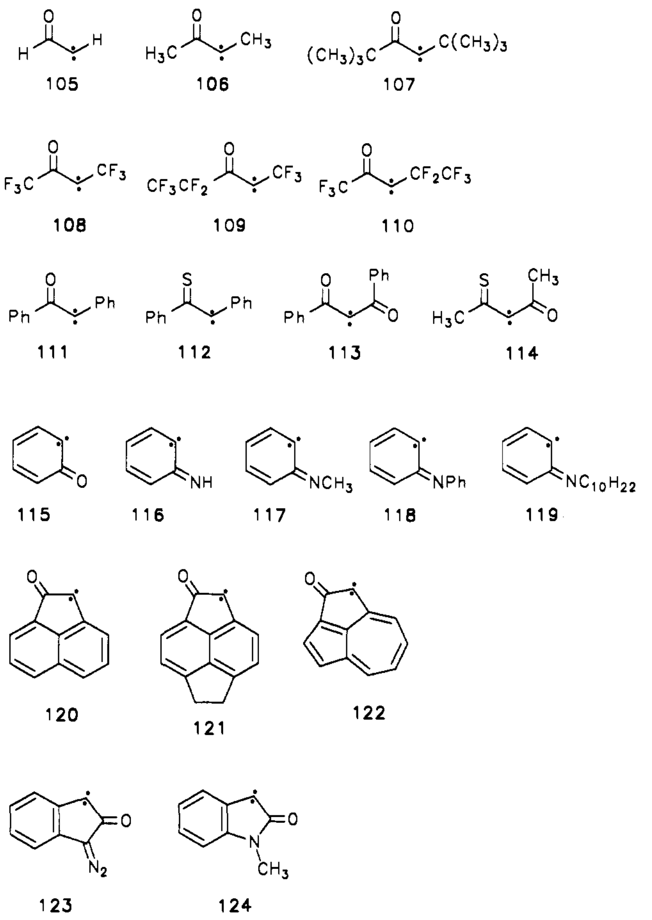
1. Ketocarbenes

ESR spectra of several ketocarbenes and related compounds have been published during the last two decades (Table IX),[184] but other spectroscopic data are quite sparse. This is mainly due to the Wolff rearrangement, which prevents the buildup of the high concentrations of carbenes necessary for IR or UV–vis work.

Formylcarbene (**105**, Chart VIII), the parent compound of ketocarbenes, has not yet been characterized experimentally. Several *ab initio* calculations on **105** and other C_2H_2O isomers have been published.[186–190] Tanaka and Yoshimine found by using Cl calculations with a double-ζ basis on the singlet C_2H_2O surface that ethynol is less stable by 36 kcal/mol than ketene, but separated by a 73 kcal/mol barrier.[187] Oxirene is 82 kcal/mol less stable than ketene, with a barrier for the oxirene–formylcarbene rearrangement of only 2 kcal/mol. An important conclusion concerning matrix isolation is that formylcarbene is unstable with respect to the rearrangement to ketene.

The role of triplet and diradical-like singlet C_2H_2O molecules in the Wolff rearrangement was explored by Novoa et al.[189] According to MC-SCF 6-31G(d) calculations singlet **105** is 1.3 kcal/mol less stable and (singlet) oxirene 4.2 kcal/mol more stable than the triplet carbene. In contrast to other *ab initio* calculations, the MC-SCF calculations predict the singlet formylcarbene to be a planar diradical with a slightly lower lying triplet. The (singlet) formylmethylene to oxirene transition state lies only 2.9 kcal/mol above triplet **105**, and thus even under the conditions of low-temperature matrix isolation, isomerization of the triplet carbene to oxirene would be facile.

Chart VIII



Hochstrasser and Wirz reported the synthesis of ethynol in Ar matrices by UV irradiation of ketene[191] or 3-hydroxycyclobutene-1,2-dione.[192] Short wavelength UV irradiation ($\lambda \leq 248$ nm) of ethynol produces ketene; other C_2H_2O intermediates such as oxirene, formylcarbene, or oxiranylidene were not observed by IR spectroscopy.

Maier et al. undertook a systematic study of the matrix photochemistry of a variety of diazoketones which under "ordinary conditions" in solution have only a small tendency for Wolff rearrangement.[193] Perfluorinated diazoketones and diazoketones with bulky substituents should be especially suitable for the generation of ketocarbenes and oxirenes in low-temperature matrices, but in all cases ketenes were the principal products of matrix photochemistry. Attempts to generate oxirenes via photochemical cycloreversion reactions in low-temperature matrices also failed.[194]

ESR spectroscopy allows detection of triplet ketocarbenes, even if the yield is very low. Strausz et al. succeeded in recording the ESR spectrum of pivaloyl-*tert*-butylcarbene (**107**) in a polycrystalline powder sample or organic glass (MCH/isopentane 4:1) at 22 K (Table IX). Irradiation ($\lambda > 300$ nm) of 2,2,5,5-tetramethyl-4-diazo-3-hexanone produced ESR signals which were stable for hours at temperatures below 50 K and decayed with first-order kinetics above 80 K.[195] The triplet spectrum was assigned to the *s-E* rotamer.

In contrast to **107**, acetylmethylcarbene (**106**) could not be detected by ESR spectroscopy under similar conditions.[195] This is in accordance with the observation that irradiation of 3-diazo-2-butanone in Ar matrices at 10 K produces both dimethyl ketene (product of Wolff rearrangement) and methyl vinyl ketone (product of 1,2-H shift).[196] The diazo ketone exists as a mixture of conformers and it was proposed that the *s-E* rotamer leads preferentially to the ketone and the *s-Z* rotamer to the ketene (Scheme IV).

The matrix photochemistry of 3-diazo-2-butanone was recently reinvestigated by Bodot et al.[197] The major photoproducts were, as described in a previous study by Strausz et al.,[196] dimethyl ketene and methyl vinyl ketone. *s-Z* and *s-E* rotamers of the latter were identified by comparison with the authentic matrix-isolated ketone. A minor product with a C═C stretching vibration at 2137 cm^{-1} was claimed to be 1,2-dimethyloxirene, which was rationalized by comparison with *ab initio* calculations. The thermal isomerization of the oxirene to the corresponding ketene was observed at temperatures as low as 25 K, suggesting a barrier of activation below 2 kcal/mol.[197b] Some evidence for the formation of ketocarbene **106** was also presented, and IR bands of very low intensity at 1096, 1032, 1028, and 758 cm^{-1} were tentatively assigned to d_6-**106**.[197a] In 1% or 5% CO-doped krypton matrices **106** was trapped presumably as methyl acetyl ketene. (Several IR absorptions were assigned to the ketene.)

Perfluoroacetylmethylcarbene (**108**) was characterized by ESR spectroscopy in organic glasses or as powder sample at 11 K (Table IX).[198] Two rotamers, *s-Z* and *s-E*, were formed in a ratio of 9:1 as primary products on irradiation of the diazo precursor. Both rotamers are stable below 50 K and the Curie law is obeyed in the range 8–50 K, indicating ground-state triplet molecules. At higher temperatures the *s-E* conformer is thermally less stable than the *s-Z* conformer. The latter decays at temperatures above 100 K with good first-order kinetics and the activation parameters were determined from the Arrhenius plots to $E_a = 5.0 \pm 0.5$ kcal/mol and $\log A = 6.5 \pm 0.9$.[198] From the low value of the preexponential factor it was concluded that ISC to singlet **108** is rate determining for the Wolff rearrangement. The rotamers do not interconvert thermally or photochemically, which suggests that the barrier of rotation is higher than the barrier of the Wolff rearrangement. The characterization of **108** by IR spectroscopy in an Ar matrix has also been claimed,[199] but later it was shown that neither carbene **108** nor the corresponding oxirene were produced in amounts which allow IR detection.[200]

Other perfluorinated ketocarbenes which were characterized by ESR spectroscopy are **109** and **110** (Table IX).[201] Again, rotational isomers *s-Z* and *s-E* were observed, with *s-Z* being formed in higher yield and being thermally more stable than *s-E*. In Ar matrices at 10 K the ketocarbenes **109** and **110** could not be observed.

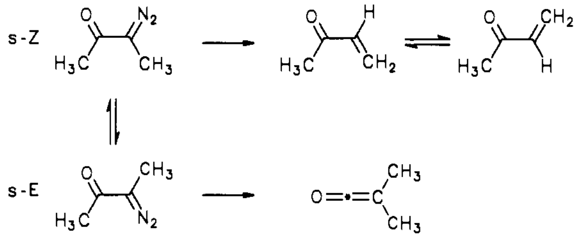
Several benzoylcarbenes have been characterized by matrix ESR spectroscopy. Benzoylphenylcarbene (**111**) was generated by irradiation ($\lambda > 345$ nm) of azibenzil in organic glasses or as powder at 77 K.[31,82,202] The ESR spectra reveal the formation of both the *s-Z* and *s-E* rotamers, which were assigned according to their ZFS parameters (Table IX).[202] The *s-Z* rotamer is the major product (>90%) and a thermal interconversion of *s-Z* and *s-E* is not observed (Scheme V). The activation barriers for the thermal decay at temperatures above

Table IX. ESR Data of Ketocarbenes (Chart VIII)

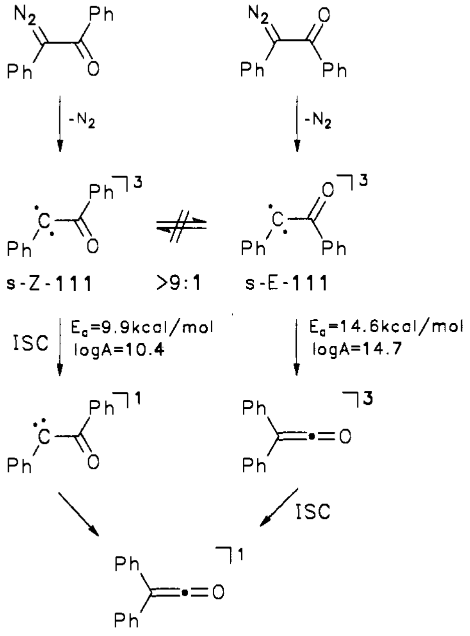
carbene	matrix[a]	T, K	D/hc, cm^{-1}	E/hc, cm^{-1}	E/D	comments	ref
107	MCH/IP (4:1)	22	0.493	0.077	0.1562	stable at 50 K	195
	neat	22	0.500	0.074	0.148		
108	neat	11	0.605	0.034	0.0562	*s-E*	198
			0.572	0.079	0.1381	*s-Z*	
109	neat	10	0.563	0.080	0.1421	*s-E*	201
			0.564	0.039	0.0691	*s-Z*	
110	neat	10	0.553	0.091	0.1646	*s-E*	201
			0.558	0.029	0.0520	*s-Z*	
111	neat	77	0.3123	0.0519	0.1662	*s-E*	202
			0.3916	0.0518	0.1323	*s-Z*	
112	neat	77	0.0318	0.00105	0.0330	stable at 77 K	223
113	neat	77	0.0801	0.0232	0.2896	*s-Z,s-E*	204
			0.029	*b*		*s-E,s-E*	
116	neat	77	0.1704	0.0025	0.0150	stable at 77 K	206
117	neat	77	0.146	*b*			206
118	neat	77	0.1150	0.0037	0.0322	*s-E*	206
			0.1054	0.0029	0.0275	*s-Z*	
119	*b*	*b*	0.13	0.004	0.0308		206
120	Ar	15	0.406	0.0264	0.0650		208
121	Ar	15	0.401	0.0253	0.0631		208
122	Ar	15	0.427	0.0179	0.0419		208
123	Ar	10	0.3631	0.0225	0.0620		209
124	HFB	4	0.38				211

[a] See Table I. [b] Not specified.

Scheme IV



Scheme V



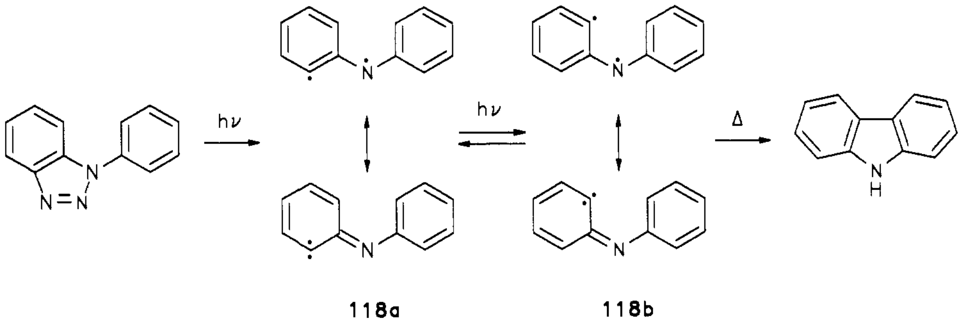
150 K (*s-Z*) and 170 K (*s-E*) were determined to E_a = 9.9 kcal/mol, log A = 10.4 and E_a = 14.6 kcal/mol, log A = 14.7, for *s-Z* and *s-E*, respectively.[202] Thus the *s-Z* rotamer is less stable than the *s-E* rotamer, and the large difference in the Arrhenius preexponential factors indicates different mechanisms for the decay. A possible explanation is the adiabatic isomerization to triplet diphenyl ketene for *s-E*, and ISC to the singlet carbene with subsequent Wolff rearrangement for *s-Z*. IR detection reveals that diphenyl ketene is the only major product in Ar matrices at 10 K.[202]

Irradiation (λ > 300 nm) of 4,5-diphenyl-1,2,3-thiadiazole powder at 77 K produced thioketocarbene **112**, which was identified by its triplet ESR spectrum (Table IX).[203] Again, the conformation of **112** is controlled by the conformation of the precursor, and consequently only the *s-E* rotamer was observed. Above 77 K **112** decays with first-order kinetics and from the Arrhenius plot values of E_a = 5.4 kcal/mol and log A = 9.1 were determined. After warming to room temperature, diphenyl thioketene was formed with a characteristic violet color.[203]

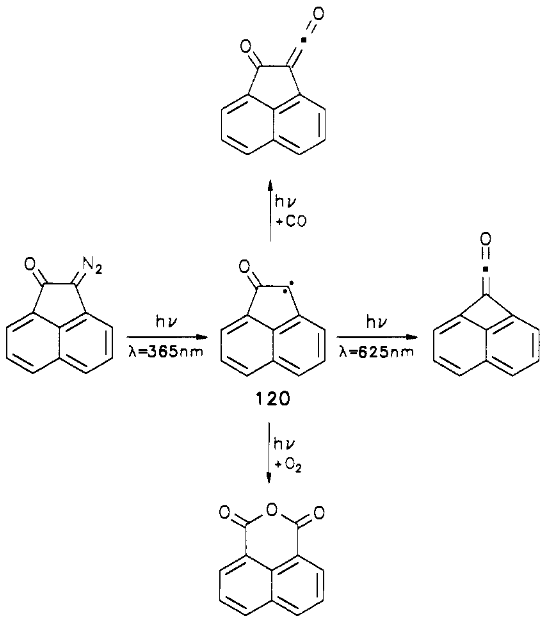
Dibenzoylcarbene (**113**) was produced by 77 K photolysis (λ > 335 nm) of dibenzoyldiazomethane powder.[204] Three conformers are possible: *s-E,s-E*; *s-Z,s-Z*; and *s-E,s-Z*. On the basis of ESR data, the *s-E,s-Z* conformer was identified as the major rotamer while the *s-E,s-E* conformer is a minor constituent. In a glass matrix only the major conformer was observed.[204] The relatively low D value observed for **113** (Table IX) has given rise to question the assignment of the ESR spectrum.[39]

While acyclic ketocarbenes can frequently be observed by ESR spectroscopy, additional electronic or steric stabilization of the carbenes relative to the ketenes is required to obtain concentrations high enough for IR detection. Wolff rearrangement of 6-oxo-2,4-cyclohexadienylidene (**115**) is very rapid, and irradiation (λ > 350 nm) of 6-diazo-2,4-cyclohexadienone in Ar at 15 K produced only cyclopentadienylidene ketene.[205] Substitution of oxygen by N–R (R = H, CH_3, Ph) gives iminocyclohexadienylidenes **116**–**119**. Carbenes **116**–**119** were generated by irradiation of the corresponding benzotriazoles as powder at 77 K and characterized by their triplet ESR spectra.[206] Two rotamers **118a** and **118b** were observed, which rapidly interconvert on irradiation, but not thermally at temperatures up to 130 K (Scheme VI). **118b** is thermally less stable than

Scheme VI



Scheme VII



118a and decays with first-order kinetics presumably to give carbazole (the sole product of solution-phase photolysis). In the range 104–124 K the activation parameters were determined to be $E_a = 5.2 \pm 0.5$ kcal/mol and $\log A = 6.5 \pm 0.8$. The low $\log A$ value indicates that ISC to the singlet carbene is rate determining and E_a corresponds to ΔE_{ST}.

The first IR spectroscopic detection of a σ-ketocarbene was reported by Chapman et al.[207,208] Acenaphthylenylidene (**120**) was generated by irradiation ($\lambda = 365 \pm 8$ nm) of 2-diazo-1(2*H*)-acenaphtylenone, matrix isolated in Ar at 15 K, and characterized by ESR (Table IX), UV–vis (λ_{max} = 621.3, 597.1, 590.3, 573.4, 563.2 nm), and IR (1665, 1015, 767 cm^{-1}) spectroscopy.[208] Irradiation at longer wavelength ($\lambda = 625 \pm 8$ nm) produces the ketene. Carbene **120** was trapped in oxygen-doped Ar matrices (20% O$_2$) to give 1,8-naphthalic anhydride, and in carbon monoxide-doped matrices (0.25%) to give the ketoketene (Scheme VII).

Ketocarbenes **121** and **122** were produced and characterized similarly (Table IX).[208] The C=O stretching modes $\nu_{C=O}$ of **121** and **122** are observed at 1658 and 1679 cm^{-1}, and the longest wavelength visible absorptions at 643 and 663 nm, respectively. In contrast to **120** and **121**, where on irradiation of the diazo precursor always a large fraction of ketene was formed, carbene **122** was produced in a very clean reaction. The Wolff rearrangement was suppressed completely, and the ketene formed only on prolonged long wavelength irradiation. These experiments reveal that ketocarbenes **120**–**122** are the primary photoproducts of the corresponding diazo ketones, and the Wolff rearrangement is induced photochemically by irradiation into long wavelength triplet–triplet absorptions of the carbenes. It was also concluded that the Wolff rearrangement is not inhibited by the ring strain of the ketenes, but rather by stereoelectronic factors in the carbenes.[208]

Tomioka et al. investigated the matrix photochemistry of 1,3-bis(diazo)indan-2-one.[209,210] The two molecules of nitrogen were split off stepwise, and ketocarbene **123** was identified by ESR (in a MTHF glass at 18 K, Table IX), IR (Ar, 8 K, $\nu_{C=O}$ 1647 cm^{-1}), and chemically by trapping with oxygen. The thermal oxygenation of **123** in 1% O$_2$-doped Ar matrices at 35 K resulted in the formation of a carbonyl *O*-oxide, which was identified by its intense O–O stretching vibration at 970 and 945 cm^{-1}.[209]

A five-membered heterocyclic carbene is 2,3-dihydro-2-oxo-1-methyl-indol-3-ylidene (**124**), which was generated by irradiation of the corresponding diazo precursor and characterized by ESR spectroscopy.[211] In solution the carbene dimerizes to give isoindigo.

2. Carboxy and Nitrile Groups at the Carbene C-Atom

Carbalkoxycarbenes are of interest for the synthesis of functionalized cyclopropanes.[212] The ESR spectra of carbomethoxycarbene (**125**) and carbethoxycarbene (**126**) (Chart IX), generated by irradiation of the diazo precursors in a variety of frozen solutions or vacuum-deposited matrices, were reported by Hutton and Roth (Tables X).[213] Matrices containing benzophenone or acetophenone gave a higher signal intensity than other matrices, which indicates that photosensitization takes place. In the temperature range 10–40 K the Curie law was obeyed, indicating a triplet ground state for **125** and **126**, while at higher temperatures the signals disappeared irreversibly. Geometric isomerism was

Chart IX

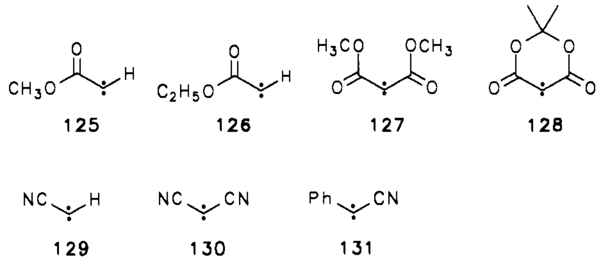


Table X. ESR Data of Carbalkoxy- and Cyanocarbenes (Chart IX)

carbene	matrix[a]	T, K	D/hc, cm^{-1}	E/hc, cm^{-1}	E/D	comments	ref
125	MCH	10	0.617	0.053	0.0859	*s*·*E*	213
			0.663	0.030	0.0452	*s*·*Z*	
126	MCH	10	0.616	0.053	0.0860	*s*-*E*	213
			0.661	0.031	0.0469	*s*-*Z*	
127	MTHF	*b*	0.604	0.031	0.0513		39
			0.606	0.051	0.0842		
			0.615	0.034	0.0553		
128	MTHF	*b*	0.578	0.035	0.0606		39
129	PCTFE	77	0.8629	0	0.0		177
130	fluorol	4	1.002	<0.002	<0.002	linear	220
	HFB	4		0.0033		bent	220
131	*b*	*b*	0.6478	0.0033	0.0219		144

[a] See Table I. [b] Not specified.

observed for both carbenes, with the *s*-*E* rotamers being formed in higher yields than the *s*-*Z* isomers. An interconversion of the isomers was not observed.[39,213]

Three different ESR spectra of dicarbomethoxycarbene (**127**) were observed after irradiation of dimethyl diazomalonate in an MTHF glass.[39] By comparison with the cyclic derivative **128**, which has a smaller *D* value than any of the *D* values determined for **127** (Table X), evidence was given that only two rotamers in different matrix sites were present in the matrix.

The ESR spectrum of cyanocarbene **129** reveals the similarity of the π-system with that of propargylene. In poly(chlorotrifluoroethylene) at 77 K the *E* parameter is zero, which indicates a linear structure.[177] A low *E* value could also be caused by motion of the H-atom in the matrix, as it has been observed for CH_2, and thus without hyperfine data the assignment of the structure is not definitive.[46,214] The UV–vis and IR spectrum of **129** and several of its isotopomers (DCCN, $HC^{13}CN$, $HCC^{15}N$), matrix isolated in Ar at 12 K, was reported by Dendramis and Leroi.[215] The normal coordinate analysis provides evidence for the linear, allenic structure, which was also deduced from the gas-phase microwave spectrum.[216] In the microwave study it was stated that an HCC angle as small as 138° would have been detected, even if the potential surface for the H–C–C bent is flat. *Ab initio* calculations both on RHF or UHF levels predict a bent triplet ground state,[217,218] while inclusion of Cl leads to a linear structure.[219] Schaefer et al. concluded from *ab initio* calculations including correlation effects that **129** is a quasilinear molecule with an H–C–C angle of ~138° and a barrier to linearity of about 2 kcal/mol.[214] Thus there is still a discrepancy between theory and experiment.

Dicyanocarbene (**130**) was generated in low-temperature matrices by UV irradiation of dicyanodiazomethane and characterized by ESR[220] and IR[221] spectroscopy. The ESR spectra in organic glasses reveal the extensive delocalization of both unpaired electrons.[220] The *E* value depends on the solvent and is <0.002 cm^{-1} in fluorolube but 0.0033 cm^{-1} in hexafluorobenzene, indicating a linear structure in the former and a slightly bent (not more than 10–15°) structure in the latter solvent. A vibrational analysis of the IR spectrum obtained in Ar at 10 K is consistent with a linear structure.[221] Again—in contrast to the experiment—theory predicts a bent structure with a C–C–C angle of 133° and a barrier to linearity of 9 kcal/mol.[222]

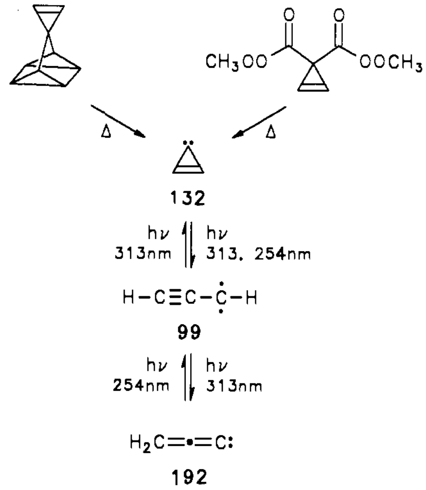
ESR data of cyanophenylcarbene (**131**) were reported.[77] The *E* value is similar to other arylcarbenes, and thus a bent structure can be deduced (Table X).

C. Cyclic Carbenes

1. Cyclopropenylidene

Recent *ab initio* calculations of C_3H_2 species predict that singlet cyclopropenylidene **132** is the global minimum of the C_3H_2 hypersurface.[224a] Maier et al. generated **132** by FVP of a quadricyclane derivative[225] or a perester[181] and subsequent trapping of the pyrolysis products in Ar at 10 K (Scheme VIII). Carbene **132** was identified by its IR spectrum and shows absorptions at 1279, 1063, 888, and 789 cm^{-1}, in excellent agreement with the calculated vibrational modes.[224,225] Additional evidence comes from the observed photochemical interconversion with propargylene **99** and vinylidenecarbene **192** (Scheme VIII, see also section III.D.2). No ESR signal was observed, which indicates a singlet ground state—again in accordance with theory. Preparative scale pyrolysis of the quadricyclane derivative produced benzene almost quantitatively, and in the presence of water the products of O–H insertion, cyclopropenol and dicyclopropenyl ether, were isolated.[225] After spectroscopic characterization in the laboratory, Thaddeus et al. were able to show that **132** is one of the most abundant molecules in interstellar molecular clouds.[226]

Scheme VIII



2. Cyclopentadienylidene, Indenylidene, and Fluorenylidene

Cyclopentadienylidene (**133**, Chart X) was one of the first carbenes to be examined by matrix isolation spectroscopy. An attempt to isolate **133** in a N_2 matrix was reported as early as 1959 by DeMore, Pritchard, and Davidson,[2] but the authors were only able to observe the dimer fulvalene. ESR data of **133** were published in 1964 by Wasserman et al.[227] The ZFS parameters [$|D/hc|$ = 0.4089 and $|E/hc|$ = 0.0120 cm^{-1}] point to a structure with C_{2v} symmetry, with one unpaired electron localized at the carbene center, while the other electron is delocalized over the five-membered ring (Table XI). Fifteen years later Baird, Dunkin, and Poliakoff reported IR and UV spectra of **133**,[29] and a full-paper,

Chart X

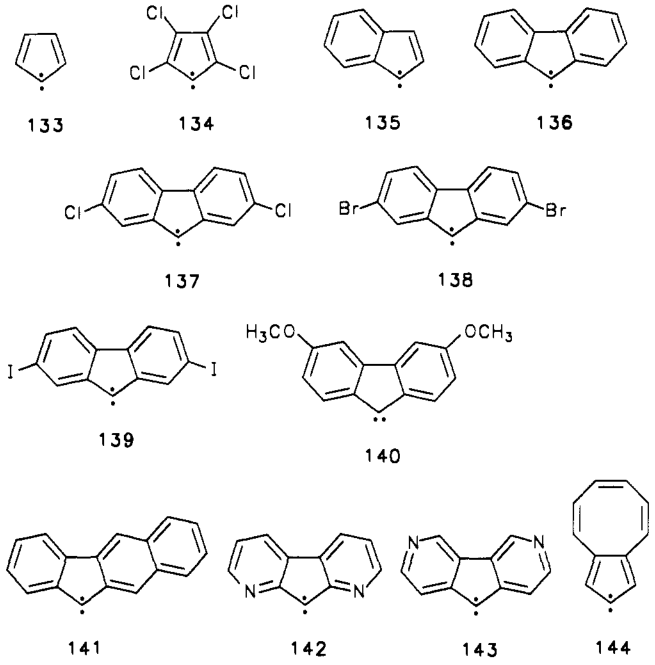


Table XI. ESR Data of Cyclopentadienylidene, Indenylidene, and Fluorenylidene Derivatives (Chart X)

carbene	matrix[a]	*T*, K	*D*/*hc*, cm^{-1}	*E*/*hc*, cm^{-1}	*E*/*D*	ref
133	HFB, HCB	4,77	0.4089	0.0120	0.0293	227
135	HFB, HCB	4,77	0.3777	0.0160	0.0424	227
136	FL[b]	77	0.4078	0.0283	0.0694	69
	DAF[c]	77	0.40923	0.02828	0.0691	95
137	MTHF	8	0.4158	0.0287	0.0690	242
138	neat	77	0.3991	0.0279	0.0699	243
	MTHF	8	0.4134	0.0281	0.0680	242
139	MTHF	8	0.4088	0.0277	0.0678	242
141	MTHF	3.8	0.39	0.030	0.077	245
142	MTHF	4	0.442	0.029	0.0656	246
143	MTHF	4	0.438	0.0306	0.0699	247
144	MTHF	17	0.2401	0.0044	0.0183	249

[a] See Table I. [b] Fluorenone. [c] Diazofluorene single crystal.

including spectroscopy with linearly polarized light, appeared in 1981.[228] The IR spectrum is relatively simple and does not exhibit particularly characteristic features (a band at 703 cm^{-1} was assigned to a C–H out-of-plane deformation mode). In the UV a broad absorption with λ_{max} at 296 nm was detected. Further matrix work on **133** dealt with its reactions with triplet oxygen[229–232] and with ethylene.[233] Tetrachlorocyclopentadienylidene (**134**) was a target of Dunkin's group in Glasgow.[234] Compared with **133**, the long wavelength absorption is red-shifted in **134** by ca. 40 nm and exhibits a distinct vibrational fine structure with spacings of approximately 1100 cm^{-1}. This vibration in the excited state is nicely reflected in the ground state with a prominent IR absorption at 1127 cm^{-1}. In the same paper, Bell and Dunkin also describe the spectroscopic properties of indenylidene (**135**).[234] Benzoannelation in **135** shifts the long wavelength UV absorption further to the red: the molecule exhibits a very weak band system between 400 and 440 nm with a sharp λ_{max} at 440 nm. The ESR spectrum, however, is less affected by the additional benzene ring; with $D = 0.3777$ and $E = 0.0160$ cm^{-1} the π-spin is only slightly better delocalized than in **133**.[227] Further matrix studies on **134** and **135** emphasized their reactions with $^3O_2$.[232,235,236]

Like many other triplet carbenes, fluorenylidene **136** was first examined by ESR spectroscopy. Values for the ZFS parameters were published by Trozzolo et al. in 1962 ($|D/hc| = 0.407$ $|E/hc| = 0.027$ cm^{-1});[68] soon after, a measurement of ^{13}C-hyperfine splitting was reported (Table XI).[69] The ZFS parameters are similar to those of diphenylcarbene; if *E*/*D* is taken as a crude measure for the amount of s character at the carbene center, the angle at the divalent carbon atom would have to range around 150°, which is not possible if one presupposes that the geometry of fluorenylidene must be similar to that of fluorene. Wasserman et al. therefore suggested "bent bonds" at the carbene center. A series of papers on ESR spectroscopy applied to **136** were to follow these early publications: Brandon et al.[95] (measurement in diazofluorene single crystal, including ^{13}C-hyperfine splitting), Barash et al.[67b] (generation of **136** from 9,9-diazidofluorene), Moser et al.[67a] (use of the sodium salt of fluorenone tosylhydrazone as photolytical carbene precursor). Electron nuclear double resonance (ENDOR) measurements on **136**, which were performed by Hutchison and Pearson,[237,238] yielded values for the spin densities in the molecule: positive spin density is found at the carbene center, at the bridgehead carbon atoms, and on C-1 and C-3.

The optical absorption spectrum of fluorenylidene, although subject of some controversy in recent years, seems to be established. In the visible range, the spectrum consists of two bands at 470 (strong) and 440 nm.[239] In order to obtain the spectrum, the measurements had to be performed at 10 K, as **136** reacts with the solvent used (MTHF) within seconds at 77 K. The matrix spectrum is consistent with the spectrum obtained by laser-flash photolysis (LFP) in acetonitrile at room temperature.[239] An absorption at 400 and 497 nm, which earlier studies[240,241] had assigned to triplet **136**, could be reassigned to a nitrile ylide and the 9-fluorenyl radical, respectively. At the same time, the early assignment of the 470-nm transition to singlet **136** had to be revised (the singlet excited state of **136** proved to be invisible in the LFP studies). Measurements in Ar matrix, performed by Bell and Dunkin[234] and by Hess,[123] resulted in the observation of UV bands at 462, 453, 436, and 251 nm (462 nm being the strongest one in the visible range), which is also consistent with the results obtained by Grasse et al.[239] in MTHF glass and in acetonitrile at room temperature, and by Closs et al.[114] (The latter only noted a similarity in the spectra of diphenylcarbene **17** and **136**, but did not give any more detailed information.)

Along with UV data in Ar matrix, Bell and Dunkin also published the infrared spectrum of **136** (absorptions at 1559, 1035, 772, 762, 755, 743, 729, and 713 cm^{-1}).[234] Somewhat different values were reported by Hess,[123] who observed bands at 1630 (s), 1418, 1215, 1025, 760 (vs), 750, 720 (vs) cm^{-1}.

A series of 2,7-dihalofluorenylidenes were the subject of work done by Schuster's group[242] and of an earlier paper by Murahashi et al.[243] The study by Rak et al.[242] was designed mainly to elucidate the question of how ground-state triplet carbenes manage to react very rapidly with typical singlet-carbene quenchers such as methanol. It failed to provide a definitive answer to this problem, but among other interesting results, it yielded valuable spectroscopic information on 2,7-dichloro-, 2,7-dibromo, and 2,7-diiodofluorenylidene (**137**, **138**, and **139**, respectively). From the ESR spectra no internal heavy-atom effect could be discerned, as the ZFS parameters of the halogenated derivatives are very close to that of parent fluorenylidene. Additionally, iodine substitution has no observable influence on the *g* values. (Significant spin–orbit coupling due to the heavy-atom effect would be expected in this case, if anywhere.) More significant substituent effects were observed in 3,6-dimethoxyfluorenylidene (**140**),[244] which, unlike almost all aryl carbenes discussed thus far, has a singlet ground state. This fact was revealed by the lack of an ESR signal in combination with completely stereospecific cycloaddition and rate constants of its reaction with methanol close to the diffusion-controlled limit. Its optical absorption spectrum in MTHF glass at 77 K is blue-shifted with respect to parent **136** (λ_{max} = 409 and 429 nm); at the same time, extinction coefficients are smaller. Another carbene with predominantly singlet chemistry in solution is 2,3-benzofluorenylidene (**141**).[245] ESR measurements in MTHF glass showed that **141** has a triplet ground state, while the combination of kinetics (laser-flash photolysis) with product studies revealed that ΔG_{ST} ($\Delta G_S - \Delta G_T$, a positive value meaning that the triplet state is lower in energy than the singlet) must be very small. (Schuster et al. reported a value of ca. 1 kcal/mol.) The optical absorption spectrum of **141** (MTHF glass, 77 K) is characterized by three bands at 485, 459, and 434 nm; it is therefore similar to that of **136**.

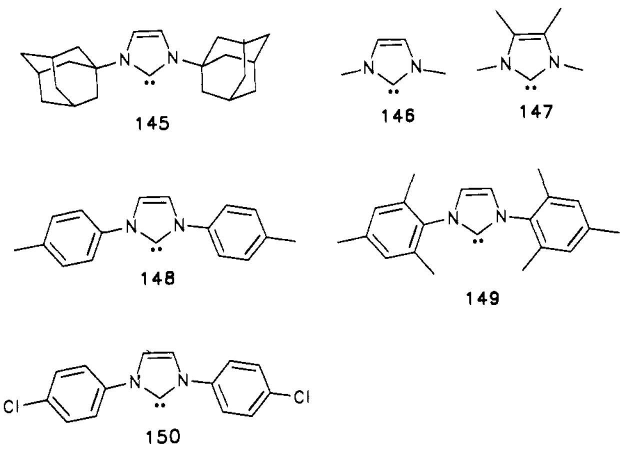
The triplet ground states of 1,8- and 3,6-diazafluorenylidene (**142** and **143**, respectively)[246–248] also exhibit only slightly different properties, if compared to triplet **136**. What makes these carbenes interesting, and in some way unique, is the unusual reactivity of their singlet excited states. So does singlet **142** react with cyclohexane at the diffusion-controlled limit, and it does not discriminate between benzene and methylstyrene. This kind of reactivity so far was only known from $^1CH_2$! In order to explain their observations, Li and Schuster therefore suggested a high proportion of π^2-character at the carbene centers in both singlet carbenes, induced by through-space and/or through-bond electronic interaction with the nitrogen atoms.

A carbene with an unusual electronic structure is bicyclo[6.3.0]undeca-2,4,6,8,11-pentaen-10-ylidene (**144**).[249] From the ESR spectrum in MTHF at 17 K a *D* value of 0.2401 cm^{-1} was obtained, which implies a large contribution of biradical character to the electronic structure of **144** (Table XI). In Ar at 12 K IR absorptions at 800 and 687 cm^{-1} and UV–vis absorptions with maxima at 546 and 506 nm were assigned to the carbene. O_2 trapping produced a carbonyl oxide with the π–π* transition red-shifted to 582 nm.

3. Imidazol-2-ylidenes

In 1962 Wanzlick was able to demonstrate that imidazolidin-2-ylidenes form a class of relatively stable nucleophilic carbenes.[250] His prediction that π-interaction leading to carbanionic centers would further stabilize the carbenes was recently confirmed by the isolation of stable imidazol-2-ylidenes. Arduengo et al. was able to synthesize several derivatives of these singlet carbenes (**145**–**150**, Chart XI), which are completely stable even at room temperature.[251,252] Although matrix isolation is not necessary for the spectroscopic characterization of these imidazol-2-ylidenes, they will be treated here because of their relation to cyclopentadienylidene (**133**) and for sake of completeness.

Chart XI



The first imidazol-2-ylidene characterized was the 1,3-diadamantyl derivative **145**, synthesized by deprotonation of 1,3-di-1-adamantylimidazolium chloride.[250] The deprotonation of imidazolium chlorides proved to be a general method for the synthesis of imidazolylidenes.[251] Carbene **145** forms colorless crystals with a melting point of 240 °C and is easily characterized by spectroscopic methods including X-ray diffraction.[250] While for **145** both electronic effects[253] and steric hindrance might contribute to the stability, the isolation of sterically unencumbered carbenes, such as **146** or **147**, demonstrates that steric factors are unimportant for the stabilization.[251] The stabilization is mainly due to a combination of the electron-donating properties of the electron-rich π-system and the σ-electron-withdrawal effect of the electronegative N atoms adjacent to the carbene center, which in turn leads to an increase of the singlet–triplet gap.[253] From X-ray diffraction studies N–C–N bond angles between 101.2° (**148**) and 102.2° (**145**) were determined, which are significantly smaller than those of the corresponding imidazolium salts. The chemistry of imidazol-2-ylidenes, although not yet studied in great detail, is also remarkable. Thus carbene **145** forms a stable ylide with iodopentafluorobenzene.[254] A thorough investigation of the chemistry of these carbenes will have a large impact on the understanding of the properties of singlet carbenes.

4. Cyclohexadienylidenes

a. 2,5-Cyclohexadienylidenes. 4-Substituted 2,5-cyclohexadienylidenes are the only cyclohexylidenes for which spectroscopic data are reported in literature. Because of very rapid 1,2-H shifts, cyclic carbenes with aliphatic α-hydrogen atoms are not stable even under the condition of matrix isolation. 2,5-Cyclohexadienylidene (**151**, Chart XII) is a benzene isomer for which experimental evidence has not been presented, so far. Jones et al. investigated the solution and gas-phase chemistry of 4,4-dimethylcyclohexadienylidene (**152**)[255] and 4,4-dimethyl-4-silacyclohexadienylidene (**153**),[256] but again spectroscopic data have not been reported

Chart XII

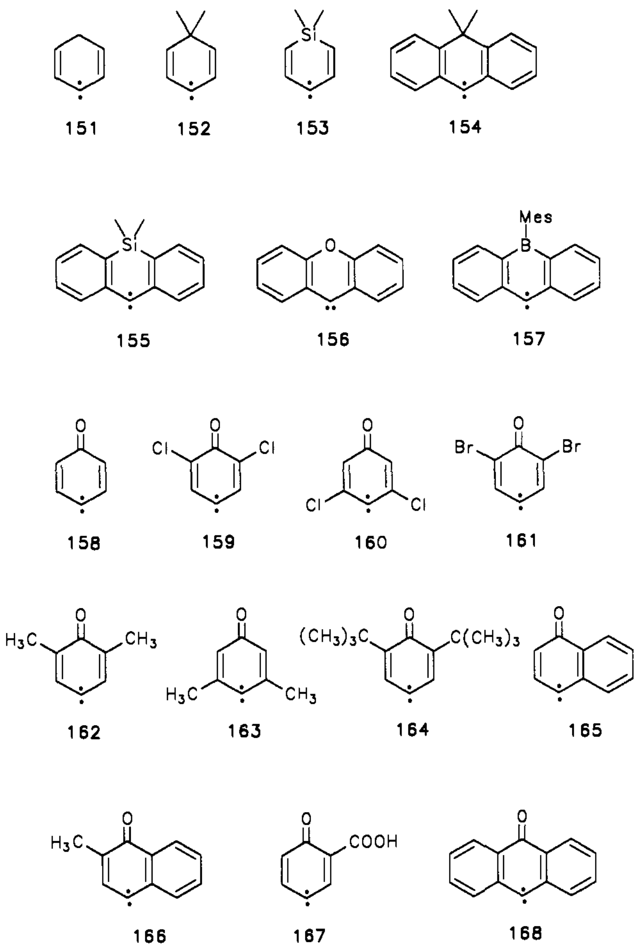


Table XII. ESR Data of 4-Oxo-2,5-cyclohexadienylidenes (Chart XII)

carbene	matrix[a]	T, K	D/hc, cm^{-1}	E/hc, cm^{-1}	E/D	ref
155[b]	EPA	40	0.391	0.0215	0.055	258
157	MTHF	4.6	0.360	0.0156	0.043	262
158	DCB	4,77	0.3179	0.0055	0.017	263
159	neat	4,77	0.3284	0.0086	0.026	263
160	TCB	4,77	0.3470	0.0010	0.0029	263
164	neat	93	0.3141	0.0051	0.016	299
165	neat	4,77	0.3333	0.0112	0.034	263
168[c]	BZP	77	0.365	0.0177	0.048	265
	neat	77	0.3638	0.0176	0.048	32

[a] See Table I. [b] Linear Curie–Weiss plot. [c] Stable at 77 K, signals disappear slowly at 160 K.

for these carbenes. From a LFP study Admasu and Platz concluded that in 10,10-dimethyl-9-anthrylidene (**154**) the singlet and triplet states are essentially degenerate.[257] ESR (Table XII)[258] as well as electronic absorption spectra (λ_{max} = 312, 345, and 510 nm)[259] of 10,10-dimethyl-10-sila-9-anthrylidene (**155**) were reported by Iwamura et al. The triplet ground state of **155** was clearly established by the observation of a triplet ESR signal and a linear Curie–Weiss plot[258] and is consistent with the rapid reaction with $^3O_2$ to form a carbonyl oxide in solution at room temperature.[260] The relatively large E value indicates a decrease of the bond angle at the carbene center.[258]

Two further hetero-substituted cyclohexadienylidenes were investigated in frozen media by Schuster et al.: 9-xanthylidene (**156**)[261] and 9-mesityl-9,10-dihydro-9-boraanthrylidene (**157**).[262] Irradiation of 9-diazoxanthene in methylcyclohexane at 77 K produced a species with UV absorptions at 393, 385, and 376 nm, which were assigned to **156**.[261] No ESR signal was observed, and from the chemical reactivity (stereospecific addition to styrenes, rapid insertion into O–H bonds and no reaction with hydrocarbons) observed in LFP and trapping experiments a singlet ground state with $\Delta G_{ST} < -4$ kcal/mol was deduced.

In contrast to **156**, triplet ESR signals, which were stable for several hours at 77 K, could readily be obtained for **157** in MTHF (Table XII). The zero-field parameters indicate that **157** is a nonlinear triplet carbene with a large one-center interaction.[262] In the UV–vis a sharp, intense band at 359 nm and broader absorptions at 460 and 530 nm are assigned to the carbene. On the basis of LFP and trapping experiments it was concluded that ΔG_{ST} in boraanthrylidene **157** is considerably larger than in fluorenylidene **136**. This is mainly a consequence of the larger bond angle at the carbene center in **157**.

b. 4-Oxo-2,5-cyclohexadienylidenes. In contrast to 2-oxo-3,5-cyclohexadienylidene (**115**), which rapidly undergoes Wolff rearrangement and therefore is not accessible to matrix isolation spectroscopy (see section III.B), 4-oxo-2,6-cyclohexadienylidene (**158**) and several of its derivatives were characterized by ESR, UV-vis, and IR spectroscopy.

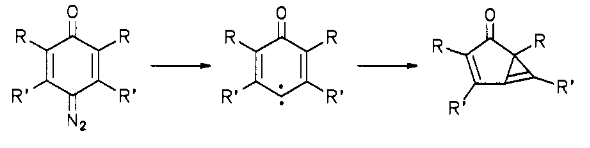
In 1964 Wasserman and Murray[263] reported the first ESR spectra of carbene **158** and several derivatives (Table XII). UV irradiation of powdered samples of the corresponding quinone diazides (either neat or as solid solution in p-dichlorobenzene) at 77 or 4 K produced carbenes **158**–**160** and **165** in their triplet ground states. The parent carbene **158** has a comparatively small D value of 0.3179 cm^{-1}, which indicates a large average distance of the unpaired electrons. One of the unpaired electrons is mainly localized in the σ-plane at carbene center C-1, as in the phenyl radical, while the other is delocalized in the π-system, as in the phenoxyl radical. The π-spin density at C-1 was estimated to approximately 0.4, similar to the para position of a phenoxy radical. The D values of the substituted carbenes are somewhat larger (Table XII). The small values of E (0.0010–0.0112 cm^{-1}) were rationalized by assuming "bent bonds" at C-1.[263] The ESR spectrum of a matrix-isolated sample of **158** is similar to that of the powder sample; between 23 and 45 K the Curie law is obeyed which proves the triplet ground state.[264]

Anthronylidene **168** was generated by photolysis of 9-diazo-10-anthrone in various organic glasses and characterized by ESR (Table XII)[32,265–268] and UV–vis[267,268] spectroscopy. In MTHF at 4 K a strong sharp UV band at 352 nm and two weak broad bands at 523 and 564 nm were found. The conclusion of these studies (including LFP experiments) was that **168** is a ground state triplet carbene with ΔG_{ST} of 5.8 kcal/mol.[268] Murai et al. reported the formation of quintet state radical pairs if the neat diazo precursor was photolyzed at low temperature.[32]

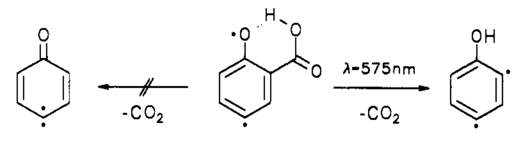
IR and UV spectra of matrix-isolated oxocyclohexadienylidenes **158**, **159**, and **161**–**167** have been reported by our group.[264,269] In the UV–vis spectra broad absorptions exhibiting vibrational fine structure around 500–600 nm and sharp absorptions at 370–380 nm are characteristic of these carbenes.[270] The former band system is rather sensitive while the sharp absorptions are insensitive to substitution. A very sharp absorption at 395 nm was also reported for the phenoxyl radical,[271] which reveals the similarity of the π-systems of this radical and the carbenes. In the IR the most characteristic absorptions are the C=O stretching vibrations in the range 1498–1558 cm^{-1}, which indicates a C=O bond order of significantly less than 2,[270] and again demonstrates the delocalization of the π-system.

Chemical evidence for the oxocyclohexadienylidenes was also given. In oxygen-doped matrices the thermal formation of carbonyl *O*-oxides was observed for all carbenes,[272,273] and for **158**, the carbonylation reaction in CO-doped matrices produced a ketene.[264,269]

The photochemistry of the carbenes—especially the vinylcarbene–cyclopropene rearrangement—was studied in some detail.[269,270] Only **162** proved to be quite stable on visible-light irradiation, while **158**, **159**, **161**, **163**, **165**, and **166** rearranged to strained 1,3-bridged cyclopropenes in yields that were highly dependent on substituents. The cyclopropenes are thermally highly labile, metastable compounds and even in Ar at 10 K they rearrange back to the carbenes quantitatively. The half-life depends on substituents, matrix, and temperature and is in the order of several weeks for the most stable benzoannelated carbenes **165** and **166** in Ar at 10 K. Irradiation with visible or infrared light also produced the carbenes quantitatively, while UV irradiation gave ketenes and other products irreversibly.



Carbene **167** readily decarboxylates on irradiation with red light (λ > 630 nm) to give *m*-dehydrophenol, while the vinylcarbene–cyclopropene rearrangement is of minor importance, only.[274]



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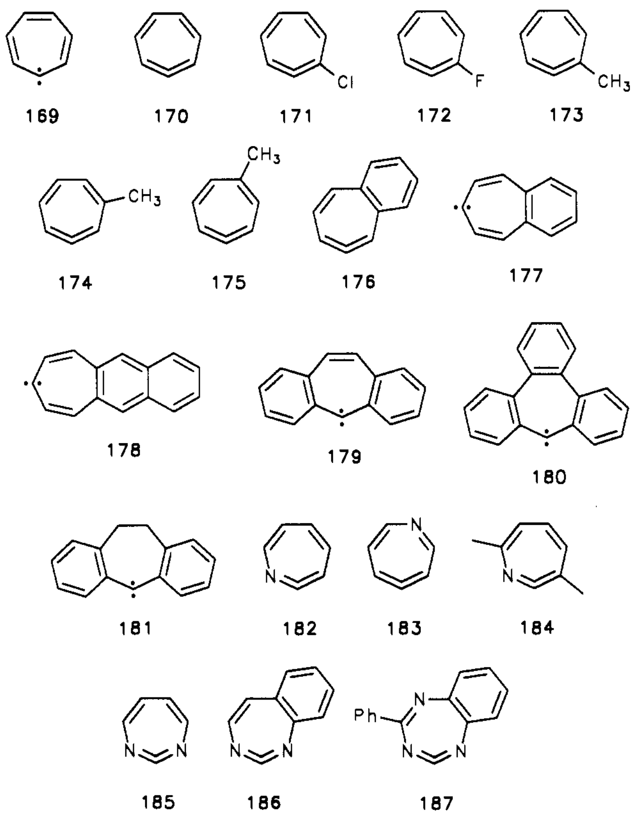
5. Cycloheptanylidenes

The C$_7$H$_6$ hypersurface, and especially the carbene/carbene rearrangement of phenylcarbene and cycloheptatrienylidene (**169**, Chart XIII), have attracted much attention during the past years. Several cycloheptatrienylidenes have been characterized spectroscopically in matrices, but still many details, e.g. the relation of **169** and cycloheptatetraene (**170**), are not yet clear. Three seven-membered ring species, which in principle can interconvert thermally or photochemically, must be considered: the planar (C_{2v} symmetry) triplet (ground state) carbene T-**169**, the planar (C_{2v} symmetry) singlet carbene S-**169**, and the nonplanar, chiral (C_2 symmetry) allene **170** (Scheme IX). Depending on the level of calculation, S-**169** is predicted to be a true minimum or a transition state between the two enantiomers of **170**.[275,276] From *ab initio* calculations Janssen and Schaefer concluded that **170** lies approximately 16 kcal/mol below S-**169**,[277] which in turn is 4.5 kcal/mol more stable than T-**169**.[277] This is in obvious contradiction to the detection of T-**169** via ESR spectroscopy (vide infra). An explanation of this is that the geometries of singlet and triplet **169** are quite different, and at the triplet equilibrium geometry the singlet lies 6.7 kcal/mol higher!

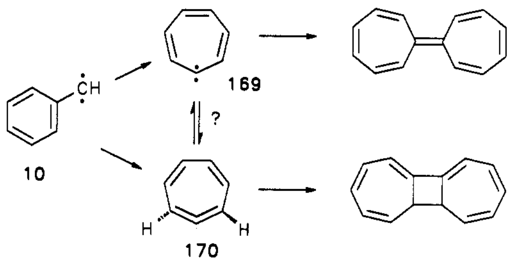
The ring expansion of phenylcarbene (**10**) to cycloheptatrienylidene (**169**) was first demonstrated by trapping heptafulvalene—the dimer of **169**—in solution experiments (Scheme IX).[278] These experiments do not rule out the formation of allene **170** as the ring-expanded product, because the dimer of **170** could thermally rearrange to heptafulvalene. Carbene **169** and cycloheptatetraene (**170**) are closely related, and therefore both isomers are treated in this chapter.

The first direct spectroscopic characterization of **170** and several of its derivatives was presented by Chapman et al. in a series of papers (Table XIV).[72,76,279-281] Irradiation (λ > 416 nm) of phenylcarbene, matrix isolated in Ar at 10 K, yielded **170** in a clean reaction.[72,280] **170** was also produced by pyrolysis of phenyldiazomethane under FVP conditions or by photolysis of a variety of other precursors (Scheme X).[279,280]

Chart XIII



Scheme IX



Scheme X

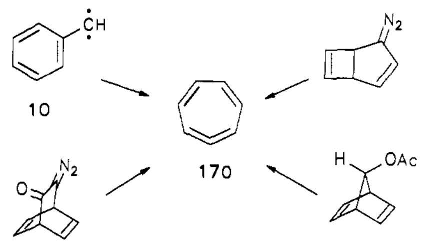


Table XIII. ESR Data of Cycloheptatrienylidene Derivatives (Chart XIII)

carbene	matrix[a]	T, K	D/hc, cm^{-1}	E/hc, cm^{-1}	E/D	ref
169	Ar	21	0.317	0.0087	0.0274	282
169	Ar	12	0.425	0.0222	0.0522	283
177	MCH, MTHF	4	0.52	0.021	0.0404	285
178	Ar	12	0.453	0.0193	0.0426	283
179	neat	77	0.3787	0.0162	0.0428	284
180	neat	77	0.4216	0.0195	0.0463	284
181	neat	77	0.3932	0.0170	0.0432	284

[a] See Table I.

Table XIV. IR Spectroscopic Data of Cycloheptatetraenes, Matrix Isolated in Ar at 10 K (Chart XIII)

carbene	C=C=C stretching, cm^{-1}	other, cm^{-1}	ref
170	1824w, 1816w	1380m	280
1-*d*-170	1822w, 1811w	1381m	280
4-*d*-170	1822w, 1815w		280
5-*d*·170	1820w, 1814w	1380m	280
171	1809m	1360w	280
172	1810m	1388m	280
3-*d*-172	1799m	1397s	280
173		1386m	281
d_3-CH_3-**173**	1819w, 1810w	1379m	281
174	1827vw, 1816w	1374m	281
175	1819w, 1811w	1379m	281
d_3-CH_3-**175**	1820w, 1810w	1366m	281
182	1895s	1348	290
183	1810		137
184	1899vw		294
185	1975s		295
186	2000s		295
187	2010s		296

The characterization of cycloheptatetraene **170** was based on spectroscopic and chemical evidence and on the results of isotopic labeling experiments.[280] The absence of a triplet ESR signal suggests a singlet ground state. In the IR weak absorptions at 1824 and 1816 cm^{-1}, which after deuteration at C-1 were only slightly red-shifted, were assigned to the allene moiety (Table XIV). Another characteristic IR absorption frequently observed in cycloheptatetraenes is a medium intensity band at 1380 cm^{-1}. The allene band was used to distinguish between **170** and bicyclo[4.1.0]heptatriene, another C_7H_6 isomer which has to be considered as an intermediate in the phenylcarbene rearrangement. For the C=C stretching mode of a strained cyclopropene, such as the bicycloheptatriene, a lower frequency and a larger deuterium isotopic shift is expected. Compelling evidence for the formation of **170** rather than bicyclo[4.1.0]heptatriene came from elegant deuterium-labeling experiments.[280] The UV–vis spectrum of **170** is not characteristic, and above 300 nm no prominent absorption was detected. After evaporating the matrix and warming to room temperature, heptafulvalene was identified as the isolable dimer of **170**.

In 1986 McMahon and Chapman[282] and Wentrup et al.[283] independently reported the first spectroscopic characterization of triplet cycloheptatrienylidene (**169**), generated by irradiation of matrix-isolated diazocycloheptatriene. The former group reported an intense triplet ESR signal with the ZFS parameters $D = 0.317$ cm^{-1} and $E = 0.0087$ cm^{-1}, indicating a planar or nearly planar structure of **169** (Table XIII).[282] Shorter wavelength irradiation irreversibly destroyed the signal. In the IR an absorption at 638 cm^{-1} and several UV–vis bands in the range 530–220 nm were assigned to **169**. It was also found that **169** neither thermally at temperatures up to 35 K, nor photochemically rearranges to **170**.

Wentrup et al. reported different ZFS parameters for **169** ($D = 0.425$ cm^{-1} and $E = 0.0222$ cm^{-1}),[283] and thus a different triplet species was observed and assigned to **169**. The Curie law was not exactly obeyed, which could mean that on warming carbene **169** partially rearranges to allene **170**. Wentrup's results are in good agreement with reported data of benzoannelated cycloheptatrienylidenes (Table XIII), but so far the important question whether there is thermal equilibration between **169** and **170** is still open to discussion. Recently Blanch and Wentrup presented evidence that Chapman's carbene is a butylated species of unknown structure,[283b] and hopefully this discussion will be settled in near future.

Several derivatives of **170** were generated in low-temperature matrices and characterized spectroscopically. Irradiation of ortho-halogenated phenylcarbenes produced 1-halocycloheptatetraenes **171**[79,280] and **172**,[280] which exhibit a substantially enhanced intensity of the allene stretching mode (Table XIV). The rearrangements of the isomeric tolylcarbenes were studied in some detail.[76,281] Methylcycloheptatetraenes **174**–**175** are key intermediates in this interconversion and the proposed mechanism also explains the isomerization of benzocyclobutene to styrene.

In remarkable contrast to phenylcarbene (**10**), 1- and 2-naphthylcarbene (**43** and **44**, respectively) did not photochemically ring expand to benzocycloheptatetraenes, but rather cyclized to benzobicyclo[4.1.0]hepta-2,4,6-trienes.[128] Deuterium-labeling experiments suggest that the cyclopropenes are the primary products and are not formed by an expansion–cyclization mechanism. Consequently, the photochemical interconversion of carbenes **43** and **44** was not observed. FVP of either 1- or 2-naphthyldiazomethane produced mainly 1*H*-cyclobuta[*de*]naphthalene[283c] and small amounts of an unknown compound, which was tentatively assigned to 4,5-benzocycloheptatetraene (**176**).[128a]

Benzocycloheptatrienylidenes **177**–**180** were generated by irradiation of the corresponding diazocycloheptatrienes and characterized using ESR spectroscopy (Table XIII).[283a,284,285] On the basis of the ZFS parameters a triplet ground state with ΔG_{ST} of 3.5–4 kcal/mol was estimated for **177**. A transient UV–vis spectrum ($\lambda_{max} = 380, 395$ nm) of this carbene was presented by Horn et al.[285] The lack of evidence for the isomeric cycloheptatetraene under the same experimental conditions was rationalized by loss of aromatic resonance energy in the allene. A similar result—destabilization of the allene relative to the carbene—was found for the naphthoannelated carbene 178[283] and is in accordance with solution studies of Hackenberger and Dürr[286] and Kirmse and Sluma.[287]

ESR spectra of carbenes **179** and **180** were reported by Moritani et al. in 1966 (Table XIII).[284] From the ZFS parameters it was concluded that **179** is planar, while **180** is substantially bent. For **179** a bond angle of 150° at the carbene center C-1 was estimated—close to the value obtained for diphenylcarbene **17**—although the internuclear angle of the seven-membered ring is smaller. This result was interpreted in terms of "bent bonds" at C-1.

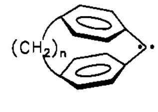
ESR[284] as well as UV–vis spectra (λ_{max} = 324, 348 nm)[113,288] of dibenzocycloheptadienylidene (**181**) were reported, and by comparison with **17** the similarity of the π-systems of both carbenes became obvious. The close relation of **181** and **17**—and the difference to fluorenylidene **136**—is a consequence of the similar bond angle at the carbene center.[288] Platz et al. studied the kinetics of H-abstraction of **181** in polycrystalline toluene at 77 K by ESR spectroscopy and were able to observe the triplet radical pair as the principal first reaction product.[289] Nonexponential decay kinetics of this reaction was attributed to matrix site effects. In perdeuterated matrices only photochemical but no thermal D abstraction was observed, indicating a large kinetic deuterium isotope effect.

Azacycloheptatetraenes (or didehydroazepines) have a similarly long and complicated history as the cycloheptatetraenes. Phenyl azide as well as pyridyldiazomethanes provide convenient entries to the C_6H_5N hypersurface. Irradiation of matrix-isolated (Ar, 10 K) phenyl azide or 2-diazomethylpyridine produced 1-aza-1,2,4,6-cycloheptatetraene (**182**, Table XIV).[290,291] In the IR an intense absorption at 1895 cm^{-1} was assigned to the N=C=C stretching mode (Table XIII). 3- and 4-diazomethylpyridine gave 1-aza-1,3,4,6-cycloheptatetraene (**183**) under similar conditions with the allene stretching mode at 1810 cm^{-1}.[137] The photochemical interconversion of the isomeric triplet pyridylcarbenes and phenylnitrene (observed by ESR spectroscopy), as well as the interconversion of the singlet species **182** and **183** was explained in a common scheme with **182** as the primary product of the phenyl azide photochemistry.[291] In contrast to the photochemistry in Ar matrices, Platz et al. found triplet phenylnitrene being the major product in rigid glasses at 77 K and proposed that **182** is produced by secondary photolysis of the nitrene.[292] This was confirmed by Hayes and Sheridan, who were able to record the IR spectrum of phenylnitrene in Ar or N_2 at 12 K. Photolysis of the nitrene finally produced **182**.[293]

Other azacycloheptatetraenes characterized by IR spectroscopy are the dimethyl derivative **184**, which was formed in very low yields only,[294] and a series of diazacycloheptatetraenes **185–187** with a strained carbodiimide group (Table XIV).[283,295,296]

6. Other Cycloalkylidenes

A group of diarylcarbenes building up on the [1.*n*]paracyclophane skeleton (**188**) were characterized by Staab, Maier, and co-workers.[297] The system, in which the carbene center was positioned in the methylene bridge, proved to be a good candidate for investigating the influence of the carbene C–C–C angle on the ESR spectra as this parameter could be changed very conveniently by varying the length of the second bridge. A small para bridge also forces the rings to be parallel and practically perpendicular to the π-carbene orbital. Correspondingly, *D* values increase upon decreasing *n* from 12 to 9; the value of 0.4787 for **188a** is one of the highest values ever reported for diarylcarbenes. It is consistent with previous findings that the triplet signals are more difficult to observe when *n* is decreased, which may be due either to a reduction in S–T splitting[298] or to a failure in detecting the corresponding carbene as the reactivity is enhanced.



188a n=9
188b n=10
188c n=11
188d n=12

D. Unsaturated Carbenes

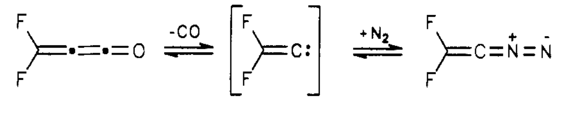
Vinylidenes and related unsaturated carbenes are highly reactive ground-state singlet carbenes of great value in preparative organic chemistry. Stang's 1978 review on unsaturated carbenes shows how broad the methods of generation and the range of reactions of these species is.[300] Nevertheless, due to the lack of appropriate photochemical precursors only a few direct experimental observations of vinylidenes and related carbenes have yet been reported. These include the infrared spectra and singlet–triplet gaps of vinylidene (**189**), fluorovinylidene (**190a**), and difluorovinylidene (**190a**), deduced from the photoelectron spectra of the corresponding vinylidene anions,[301] and the very remarkable matrix isolation studies of Maier et al. on the interconversion of C_3H_2 isomers.[180,181,225]

1. Vinylidene

Singlet vinylidene (**189**) was calculated to be a shallow minimum on the C_2H_2 potential energy surface.[302–307] The activation energy for the rearrangement to acetylene is very small, and one of the most recent values obtained by means of high level *ab initio* theory was as low as 0.9 kcal/mol.[305] A higher barrier was estimated for the excited triplet state of **189**.[302,308] Several gas-phase studies on **189** have been published,[309–311] but because of the low barrier toward rearrangement matrix isolation has not been possible.

From the photoelectron spectrum of the fluorovinylidene anion the hydrogen isomerization barrier for **190a** was estimated to 2 ± 1 kcal/mol,[301b] in good agreement with theory.[303] For difluorovinylidene **190b**, on the other hand, a much higher barrier was calculated,[312–314] and several experimental investigations concerning this molecule were published.[301b,315,316] Brahms and Dailey investigated the photochemistry of difluoropropadienone in Ar and N_2 matrices.[316] Difluoropropadienone proved to be inert on short wavelength irradiation (λ > 185 nm) in solid Ar, but in N_2 matrix produced difluoroacetylene, CO, and small amounts of difluorodiazoethene (Scheme XI). In a CO-labeled N_2 matrix the carbonyl group of [1-^{13}C]difluoropropadienone was exchanged on irradiation, however, no trace of **190b** was detected in the IR spectra. According to *ab initio* calculations the reaction of **190b** with CO as well as with N_2 is strongly exothermic, which explains the difficulty of observing the carbene in the

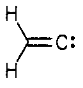
Scheme XI



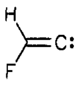
190b

presence of these molecules in the same matrix cage. Recently Lineberger et al. reported vibrational frequencies of singlet **190b** at 1670, 905, and 510 cm^{-1}, obtained from the photoelectron spectrum of the difluorovinylidene anion.[301b]

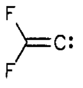
Cyclopentadienylidenecarbene (**191**) is an isomer of benzyne and was subject of experimental[317] semiempirical,[318a] and *ab initio*[318b] studies. The thermal interconversion of benzyne and **191** has been claimed,[317b–d] but so far no definitive experimental evidence for this rearrangement, nor any spectroscopic data of **191** have been presented.[317a] According to *ab initio* calculations **191** lies 31 kcal/mol above benzyne and is bound by less than 5 kcal/mol.[318b] Thus, matrix isolation of this carbene is a real challenge.



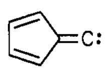
189



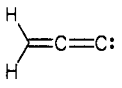
190a



190b



191



192

2. Vinylidenecarbene

Maier and co-workers were able to demonstrate that the three C_3H_2 isomers cyclopropenylidene (**132**), propargylene (**99**), and vinylidenecarbene (**192**) interconvert photochemically in low-temperature matrices (Scheme VIII).[180,181,225]

Vinylidenecarbene (**192**) is the sole derivative of vinylidene isolated to date in a matrix and characterized by spectroscopic methods. The most intense absorptions of **192** were observed at 1952 and 1963 cm^{-1} and assigned to the antisymmetric C=C=C stretching vibration. The assignment of IR data was supported by deuteration (both the mono- and dideuterio derivative were synthesized) as well as by calculations using high level *ab initio* methods (MP2/6-31G(d,p)).[182,224a,319] Irradiation of matrix-isolated cyclopropenylidene (**132**) with 313-nm light rapidly produced propargylene **99**, which on further irradiation (20 h) gave vinylidenecarbene (**192**) in almost quantitative yield. At 254 nm, the isomerization was reversed to give **99**, which again could be converted to **192** and small amounts of **132**.

3. Carbon Oxides C_nO and Suflides C_nS (with $n > 1$)

Carbon oxides C_nO and sulfides C_nS are expected to have singlet ground states for odd numbers *n* of carbon atoms, and triplet ground states for even numbers. There are two principal ways to synthesize these molecules in matrices: the thermal or photochemical carbonylation of carbon atoms or molecules C_{n-1}, generated by evaporation of graphite with subsequent trapping in low-temperature matrices, or the photolysis or vacuum pyrolysis of suitable precursor molecules, such as diazoketones or thiadiazols.

C_2O was prepared either by photolysis of carbon suboxide C_3O_2 or by the reaction of carbon atoms and CO,[322a] and characterized by IR, UV–vis, and ESR spectroscopy in various matrices.[322a,b] The three fundamental vibrations of C=C=O were observed at 1978, 1074, and 381 cm^{-1}, and on the basis of isotopic labeling a linear structure was deduced.[322a] This was confirmed by ESR data, which are in accordance with a linear triplet ground state molecule.[322b] The ZFS parameter *D* was much depending on the matrix, varying between 0.7392 cm^{-1} in neon and 0.454 cm^{-1} in xenon. The decrease of *D* in the heavier noble gas matrices was explained by spin–orbit mixing-in of singlet states via the matrix. On annealing matrices containing both C_2O and CO at 35 K carbon suboxide was produced, indicating a very low activation barrier for this reaction.[322a]

C_3O was synthesized by trapping of carbon atoms with CO,[322c] by FVP of fumaroyl dichloride with subsequent trapping in argon at 10 K,[322d] and by photolysis of C_4O_2, generated from cyclic diazoketones.[323a] Fundamental vibrations of C_3O were observed at 2242.6 (ν_1), 1907.2 (ν_2), and 579.6 (ν_4) cm^{-1}.[322d] The high frequency of ν_1 indicates a partial triple bond character of the C–O bond. A small C–C–C bending force constant (and a rather anharmonic bending potential) was obtained from normal coordinate analysis.

Maier et al. were able to produce C_3S by photolysis of OC_4S (splitting off CO) or SC_4S (splitting off CS) in argon matrices at 12 K.[323b] Fundamental absorptions at 2046.2 (ν_1), 1533.2 (ν_2), and 725.6 (ν_3) cm^{-1} were in good agreement with the expectation from theory.

C_4O is the principal photoproduct (230-nm irradiation) of matrix-isolated C_5O_2.[323c] Intense IR absorptions were found at 2221.7 and 1922.7 cm^{-1}, and weak absorptions were found at 1431.5, 774.8, and 484.0 cm^{-1}, as expected from *ab initio* calculations. Maier et al. were also able to generate C_7O_2 by flash vacuum pyrolysis of mellitic acid anhydride.[323d] Irradiation of C_7O_2 produced a new species with IR absorptions at 2163.8 and 1447.8 cm^{-1}, which was identified as C_6O.

Mixtures of C_4O and C_6O were also produced by irradiation (405 nm) of matrix-isolated carbon molecules (C_3 and C_5) in the presence of CO.[323e] These carbon oxides were predicted to have triplet ground states, and the observation that they were formed photochemically, but not thermally, was taken as hint for a spin-forbidden reaction between CO and (singlet) C_3 and C_5, respectively. The ESR spectra are in accordance with linear triplet ground-state molecules. In neon matrices at 4 K ZFS parameters *D* of 0.759 for C_4O and 1.10 for C_6O were observed.[323e]

E. Heterofunctions at the Carbene C-Atom

A number of carbenes with electronegative substituents, especially halogen and oxygen, have been characterized in matrices, but only a few examples of carbenes with electropositive elements attached to the carbene center are known. Due to the stabilization of an empty carbene p orbital by electron-donating heteroatoms, the ground state of carbenes bearing halogen, oxygen, or other electronegative elements with nonbonding electron pairs at the carbene carbon is singlet. The singlet–triplet gap of heterosubstituted methylene derivatives was the subject of recent *ab initio* studies.[320,321] Electron paramagnetic resonance, a powerful analytical tool in the case of triplet carbenes, is no longer possible, and only vibrational and electronic absorption and emission spectra can be recorded. Thus, in general, higher concentrations of singlet carbenes are necessary for spectroscopic detection. In the 1960s and 1970s, research focused on triatomic halocarbenes, while after 1980, matrix infrared and UV–vis spectra of heterocarbenes with larger organic substituents were reported.

1. Triatomic Halocarbenes

Matrix isolation studies of methylene derivatives with one or two halogen substituents cover 10 of the 14 possible structures ranging from CHF to CI_2. CHBr, CHI, ClCl, and ClBr have not been reported, yet, and CI_2 was not detected with certainty. The majority of this research was conducted in a few laboratories, especially by the groups of Jacox and Milligan, Andrews, and Bondybey. A variety of experimental techniques were applied, including photolysis of difluorodiazirine,[324] pyrolysis,[325–331] and photolysis[325] of organic and organometallic halides, reaction of alkali metals with halomethanes,[327,331–337] reaction of carbon atoms with halogens[338,339] and hydrogen halides,[340] Ar microwave discharges,[341] and hydrogen[324a,342–350] and noble gas[351–355] resonance VUV photolysis of halomethanes. Also, halomethylenes are byproducts when halomethanes are exposed to excited Ar atoms[356] or proton beam[357–359] irradiation. In some cases structures and valence force potentials were derived from spectroscopic data.[332,336,338,340,342,343,346,349] A table with molecular constants of five dihalocarbenes including ground- and upper-state normal mode frequencies, the (0,0,0–0,0,0) transition, and lifetimes has appeared in ref 344.

Little has been reported on chemical reactions of the triatomic halocarbenes in matrices. Most of the work focuses on physical properties of ground and excited states like vibrational constants and structure parameters. Therefore, only a short summary of the literature and the experimental techniques applied will be given here (Table XV).

CF_2, in most cases generated from difluorodiazirine[324] or by VUV photolysis of methylene fluoride,[324a,347,354] was the first[341] halocarbene that could be trapped in a matrix, and it is the only dihalocarbene that allows direct IR observation of the bending mode absorption. It was characterized by absorption[324b,324c,328,338,341] and emission[324a,347] spectroscopy. CF_2 does not react with CO_2 or CO under matrix isolation conditions,[324c] but was shown to yield the free-radical CF_3 when reacted with F atoms.[324b] It was also detected after VUV photolysis of methyl fluoride,[343] which was interpreted as the result of the reaction of F atoms with CF. CCl_2 was generated by many different methods including reaction of carbon atoms with chlorine,[339] reaction of alkali metals with halides,[327,335–337] pyrolysis of organometallic compounds,[326,327,329,330] VUV photolysis of methylene chloride[346,348,349] and CCl_4,[353] and pyrolysis or photolysis of dichloroketene.[325] It was characterized by absorption[325–327,329,330,336,339,349,353] and emission[335,337,346,348] spectroscopy. It was also described as a byproduct in numerous studies dedicated to ions or radicals.[333,352,356–359] In a similar way CBr_2 was characterized by absorption[332,333,357] and emission[337,344] spectroscopy, and was reported as a byproduct[352,353,359] in several other studies. So far no proof of the existence of CI_2 is available.[331,337] Fluorocarbene CHF[343,351,354] and chlorocarbene CHCl[340,349] were generated by the reaction of carbon atoms with the corresponding hydrogen halides, or by VUV photolysis of organic halides. Polyhalomethanes are suitable photoprecursors of the mixed dihalocarbenes CFCl,[334,342,345,350–352] CFBr,[351,352,355] and CFI.[351] CClBr[326,332,337,344,357,359] was prepared by several different methods including reaction of metal atoms with halomethanes[332,337] and pyrolysis of a mixed phenyl mercury compound.[326] Except for CFI, which was studied by IR only, the mixed dihalocarbenes were characterized by both absorption and emission spectroscopy.

Table XV. IR Spectroscopic Data of Dihalocarbenes, Matrix Isolated in Ar

	ν_1, cm^{-1}	ν_2,[a] cm^{-1}	ν_3, cm^{-1}	ref(s)
CF_2	1222	668	1102	324c,338
$^{13}CF_2$	1191	(665[b])	1073	324c,338
CCl_2	718,721	(326,[c]333[d])	748	336,339,349
$^{13}CCl_2$	697,700	(325[c])	726	336,339,349
CBr_2	595	(196[e,f])	640	332
CI_2			535?,525?	331
CHF		1405	1181	343,354,351
^{13}CHF		1401	1154	343,351
CDF		1046	1183	343,351
CHCl		1201	806–815[g]	340,349
$^{13}CHCl$		1197	783–791[g]	340,349
CDCl			796–805[g]	340,349
$^{13}CDCl$			778–787[g]	340
CFCl	1146	(445,[h]442[i])	742,739	342,351
$^{13}CFCl$	1120		718,716	342,351
CFBr	1157	(340[j])	647,656,659	351,352
CFI	1121,1133		573,576,583	351
CClBr	739	(257,[k]260[l])	612	326,332

[a] Bending modes (ν_2) derived from electronic spectra are included in parentheses. [b] Reference 354. [c] Reference 335. [d] Reference 348. [e] Reference 337. [f] Reference 344. [g] Quartet. [h] Reference 334. [i] Reference 350. [j] Reference 355. [k] Reference 337. [l] Reference 344.

2. Aryl- and Alkylhalocarbenes

Owing to the work of Graham[360] in 1965, halodiazirines are now widely used as photochemical precursors of alkyl- and arylhalocarbenes (Scheme XII).

The best-known arylhalocarbene is phenylchlorocarbene[12,79,280,361–366] (**193**, Chart XIV), whose diazirine precursor is easily synthesized from commercially available benzamidine hydrochloride. Infrared spectra in Ar matrices[79,280,364,365] as well as UV–vis spectra (Table XVI) in Ar[79] and in organic glasses[12,361,363] of carbene **193** have been published. In the IR-intense absorptions at 1590, 1225, 1170, 848, and 735 cm^{-1} were assigned to the carbene.[365] The UV absorptions observed at 307 and 282 nm in an organic glass (3-methylpentane)[361]

Scheme XII

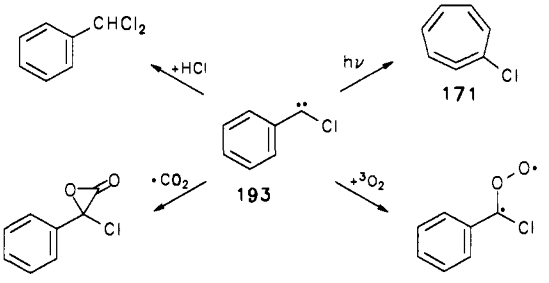
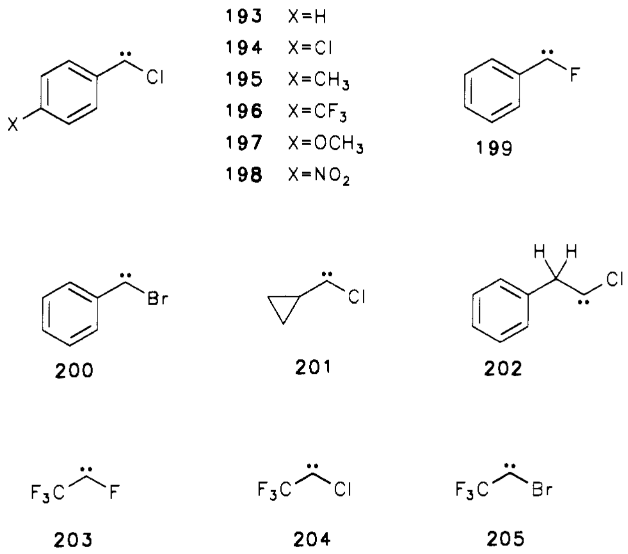


Chart XIV



are shifted to 298 and 276 nm, respectively, in solid Ar.[79] In the ESR no signal was observed, which provides evidence for a singlet ground state. On short wavelength irradiation (λ > 338 nm) **193** rearranges to 1-chlorocycloheptatetraene (**171**).[79,280]

The chemistry of carbene **193** in rigid media has been studied quite extensively. In 1982, Tomioka et al. were able to show that the reactivity of **193** toward alcohol and alkenes shows no significant change in glassy matrices at 77 K compared to its ambient temperature chemistry. No increase in H-abstraction products was observed, which was taken as evidence for the carbene's singlet ground state.[362] In an Ar matrix doped with HCl, carbene **193** readily reacted to give benzal chloride on warming to 38 K.[365] In an O_2-doped Ar matrix the carbene was slowly (6 h at 35 K) transformed to the yellow-green benzoyl chloride *O*-oxide.[365] This is in contrast to the rapid oxidation of triplet carbenes under the same conditions and reveals the spin restrictions on this reaction.[79] Carbene **193** was also shown to react with CO_2 to produce an α-lactone in cryogenic matrices.[366]

Phenyl-substituted phenylchlorocarbenes **194–197** were isolated in solid 3-methylpentane at 77 K and characterized by their UV–vis spectra (Table XVI).[12] (*p*-Nitrophenyl)chlorocarbene (**198**) was shown to react in doped Ar matrices with O_2 and CO_2 to give the carbonyl oxide and α-lactone, respectively.[366] The oxidation of **198** is faster, while the carboxylation is slower than the corresponding reactions of **193**, which indicates an electrophilic attack in the former reaction, but that in the latter system a nucleophilic attack of the carbene is rate determining. By comparison of the rates of carboxylation with that of **193** and diphenylcarbene **17** it was shown that it is not the spin state, but rather the philicity of the carbenes that is the rate-determining factor in this reaction.[366]

UV spectra of fluorophenylcarbene (**199**, λ_{max} 270) and bromophenylcarbene (**200**, λ_{max} 328) were recorded in MP glass at 77 K and compared to transient spectra obtained in LFP experiments (Table XVI).[363] Fluorophenylcarbene (**199**) was also identified by IR spectroscopy and shown to rearrange to cycloheptatetraene (**172**) on irradiation in solid Ar.[280]

Table XVI. UV–Vis and IR Spectroscopic Data of Halo- and Oxycarbenes (Charts XIV and XV)

carbene	matrix	T, K	UV λ_{max}, nm	IR, cm^{-1}	ref(s)
193	Ar	10	300	1590,1225,1170,848	365
193	MP	77	308		361
194	MP	77	323		12
195	MP	77	317		12
196	MP	77	303		12
197	MP	77	346		12
198	Ar	10		1601,1588,1206,831	366
199	MP	77	270		12,363
200	MP	77	328		12,363
201	N_2	14	460,240	1346,921,852	58
202	Ar	10	304		59
203	Ar	12	465,235	1286,1226,1159,1152	367
204	Ar	12	640,235	1238,1186,1154,920	367
205	Ar	12	665,270,235	1229,1178,1147,858	367
206	N_2	12	360	1343,1374	372
207	N_2	20	396	1396	373
208	Ar, N_2	10	318	1310(*s*·*E*),1300(*s*·*Z*)	376
209	N_2	12	245	1462,1442,603	377
210	Ar, N_2	10	320	1251(*s*-*E*),1285,1275(*s*·*Z*)	378
211	N_2	10	390	1330,1320,1288,1275	379
212	MP	77	255		381

Cyclopropylchlorocarbene[58] (**201**) was the first alkylhalocarbene to be observed by infrared spectroscopy (see section III.A.2), and in this case no thermal rearrangement (1,2-[H]- or 1,2-[C]-shift) was observed under the conditions applied. When cyclopropylchlorodiazirine was photolyzed in a nitrogen or an Ar matrix at 12 K, **201** was formed in good yield along with the carbon shift product, and the carbene could be thermally trapped with HCl by warming the matrix to 38 K.[58] Rearrangement to chlorocyclobutene occurs—due to the electronic stabilization caused by the cyclopropane ring—only upon irradiation.

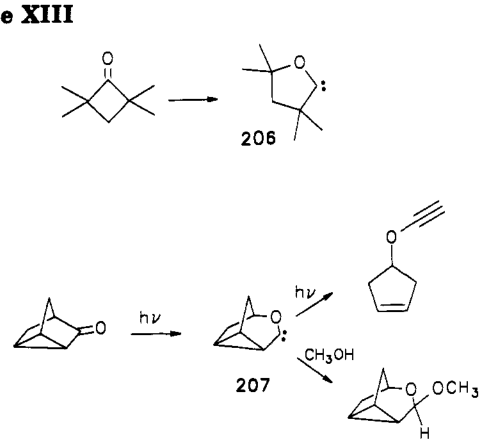
The thermal 1,2-[H]-shift could be followed in the case of benzylchlorocarbene (**202**) and at its isotopomer deuterated at the benzylic positions.[59] In this case the deuterated carbene is stabilized due to a deuterium kinetic isotope effect, and thus much higher concentrations than with the nondeuterated carbene were obtained in an Ar matrix.

The (trifluoromethyl)halocarbenes (**203–205**) were subjects of a recent matrix isolation study combined with *ab initio* calculations of infrared and UV–vis spectra (Table XVI).[367] The observed rather long wavelength absorptions in the visible region were taken as evidence for the singlet ground states of these halocarbenes. Broad-band irradiation (λ > 280 nm) of the carbenes produced trifluorohaloethenes. In N_2 matrices carbene **205** was found to add N_2 photochemically to form bromo(trifluoromethyl)diazomethane.

3. Oxycarbenes

The parent oxycarbene, hydroxycarbene, was suggested as an intermediate in formaldehyde photolysis[368] and in the reaction of carbon atoms with water[369,370] but has never been directly detected. In 1974 a first trace of an oxycarbene UV absorption was reported by Quinkert and co-workers, who photolyzed substituted cyclobutanones in glassy matrices.[371] In the UV, absorptions with maxima around 360 nm were tentatively assigned to the carbenes. These experiments were recently repeated by Matsumura, Ammann, and Sheridan, providing further proof for the oxycarbene formation.[372] Irradiation (λ = 284 nm) of 2,2,4,4-tetramethylcyclobutanone, matrix isolated in N_2,

Scheme XIII

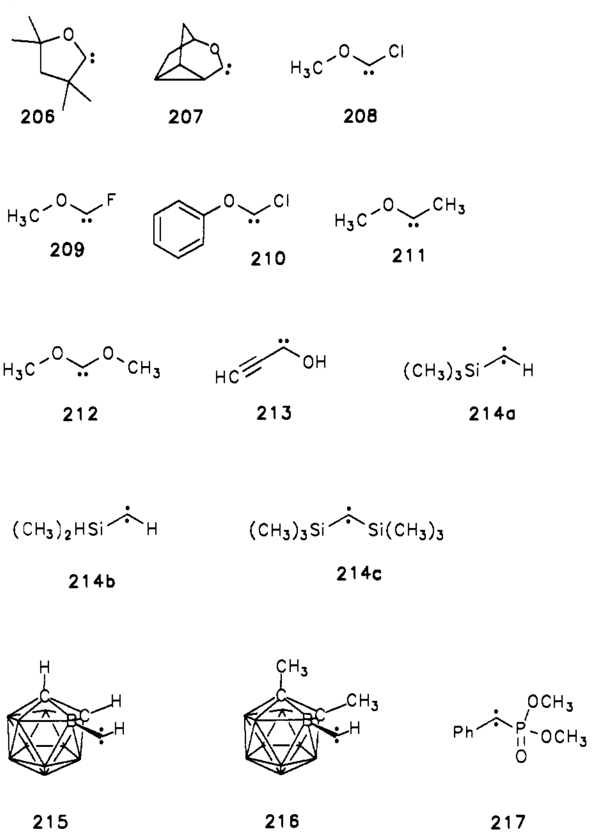


produced carbene **206** with strong IR absorptions at 1343 and 1374 cm^{-1} and a UV absorption with λ_{max} of approximately 360 nm. Trapping experiments in organic glasses (MP) containing methanol confirmed this assignment and the earlier experiments of Quinkert et al. Similarly, tricyclic oxycarbene **207** was formed on UV irradiation (λ = 285 nm) of nortricyclanone in N_2 at 20 K.[373] Carbene **207** was characterized by its IR and UV absorptions (Table XVI) and could be trapped by methanol to give the corresponding acetal. Broad band irradiation (λ > 270 nm) lead to an increase of nortricyclanone—indicating that the ring expansion of the ketone is reversible—and of a terminal acetylene (Scheme XIII). The ring expansion of cyclobutanones to give oxycarbenes was also the subject of a number of *ab initio* calculations.[372,374,375]

Sheridan et al. described the matrix isolation and characterization of a number of oxygen-substituted carbenes (**208**–**211**, Chart XV), generated by photolysis of the corresponding oxydiazirines. All carbenes were isolated in N_2 or Ar matrices and characterized by IR and UV spectroscopy (Table XVI). Careful analysis of the spectra revealed considerable C–O double bond character and the presence of geometrical isomers in all cases.

Methoxychlorocarbene (**208**) is a typical example of an oxycarbene, and a vibrational analysis based on isotopic labeling and comparison with chloromethyl methyl ether and methyl chloroformate as model compounds was presented.[376,413] On ^{18}O-labeling, two IR absorptions (at 1300 and 950 cm^{-1}, respectively) exhibited large isotopic shifts, and were assigned to the antisymmetric and symmetric C–O–C stretching mode of the *cis*-carbene, indicating the partial double bond character of the C–O bond. A strong absorption at 690 cm^{-1} was assigned to the C–Cl stretching mode. A second set of absorptions at 1310 and 774 cm^{-1} exhibited a different wavelength dependence of the photochemistry and was assigned to the *trans*-carbene.[376] Irradiation at 370 nm caused more rapid destruction of the *trans*-carbene, while upon 290-nm irradiation the *cis*-carbene was more rapidly photolyzed. The principal photoproducts of **208** in Ar were acetyl chloride, ketene, and HCl, while in N_2 traces of methyl chloride and CO were also observed. This is in contrast to the room temperature decomposition of the carbene which produces mainly methyl chloride and CO. More evidence for carbene **208** was provided by trapping experiments with HCl, which produced dichloromethyl methyl ether, and from the direct IR observation of the dimerization of **208** in MP glass at 80 K.

Chart XV



Geometrical isomers, indicating significant double bond character for the C–O bond, were also observed for methoxyfluorocarbene (**209**),[377] phenoxychlorocarbene (**210**),[378] and methylmethoxycarbene (**211**).[379] On further irradiation, these carbenes rearrange to the corresponding carbonyl compounds, accompanied by loss of CO and hydrogen halide.

Methylmethoxycarbene (**211**) is one of the few carbenes bearing α-H atoms that could be characterized in low-temperature matrices. The carbene could be trapped in a methanol/2-methylbutane glass at temperatures as high as 80 K, which is in accord with *ab initio* calculations[380] predicting a barrier of more than 20 kcal mol^{-1} for the [1,2]-H-shift in (alkyloxy)carbenes. Photolysis (λ > 340 nm) of **211** in an N_2 matrix produced acetone (product of methyl shift), methyl vinyl ether (product of H-shift), ketene, and methane, the latter formed by fragmentation and rearrangement.[379] Dimethoxycarbene (**212**) was spectroscopically characterized by its UV–vis absorption in a MP glass at 77 K (Table XVI).[377,381]

Hydroxyethynylcarbene (**213**) and its ^{18}O-isotopomer were produced by the reaction of C_3 carbon clusters with matrix-isolated water and characterized by IR spectroscopy (C≡C stretching mode at 1992.8 and 1999.8 cm^{-1}).[382] Photolysis of the carbene caused isomerization to propynal.

4. Heterocarbenes with Electropositive Substituents

In contrast to the rich chemistry of carbenes bearing electronegative substituents, only few carbenes with electropositive substituents have been investigated experimentally. The photochemistry of (trimethylsi-

Table XVII. ESR Data of Silylcarbenes and Carboranylcarbenes

carbene	matrix	T, K	D/hc, cm^{-1}	E/hc, cm^{-1}	E/D	ref
214a	Ar	4	0.613	0.00145	0.002	383b
214b	Ar	4	0.628	0	0	383b
214c	Ar	4	0.614	0.00252	0.004	383b
215	MCH	10	0.657	<0.002	<0.003	385b
216	MCH	10	0.661	<0.002	<0.003	385b
217	Ar	10	triplet			386

lyl)diazomethane in Ar matrices was reported by both Chapman et al.[383a] and Chedekel et al.[383b] 2-Methyl-2-sila-2-butene (1,1,2-trimethylsilene) was the principal product characterized, while (trimethylsilyl)carbene (**214a**) was not detected by IR spectroscopy. Attempts to trap **214a** with molecular oxygen also failed,[384] which indicates that the carbene is either short-lived under the conditions of matrix isolation—which we feel is unlikely—or does not survive photolysis of the diazo precursor. Irradiation with short wavelength UV light (250 nm) finally produced dimethylvinylsilane.[384]

Although these IR experiments did not provide direct evidence for the formation of carbene **214a**, an ESR spectrum typical of a ground-state triplet carbene could be obtained in solid Ar (Table XVII).[383b] This means that at least small amounts of the carbene are formed and are stable in the matrix. Similarly, ESR spectra of dimethylsilylcarbene (**214b**) and bis(trimethylsilyl)carbene (**214c**) were recorded (Table XVII).[383b] From the very small E values a linear structure of α-silylcarbenes was deduced, which was rationalized by an p_π–d_π overlap between the carbene carbon and adjacent silicon atom.

3-*o*-Carboranylcarbenes **215** and **216** are the first boron-substituted carbenes that have been characterized spectroscopically.[385] Trapping experiments in solution provided evidence that **216** is a triplet ground state carbene with enhanced triplet activity.[385a,c] This was confirmed by the observation of a linear Curie plot in the ESR for both **215** and **216** over the range 14–30 K.[385b] The small ZFS parameter E was taken as evidence for a linear structure of both carbenes (Table XVII), in accordance with semiempirical MNDO calculations.

The isolation of phosphonylphenylcarbene (**217**) in Ar at 10 K was recently reported by Tomioka et al.[386] IT absorptions at 1268, 788, and 536 cm^{-1} were assigned to the carbene. Carbene **217** proved to be very photostable, compared to other phenylcarbenes and did not rearrange to a cycloheptatetraene even under prolonged short wavelength UV irradiation. Annealing of O_2-doped matrices at 35 K readily produced the carbonyl oxide while the formation of the ketene in CO-doped matrices at the same temperature was considerably slower. This behavior was also observed with other triplet carbenes and attributed to spin restrictions in formal "spin-forbidden" reactions.

In a series of papers Bertrand et al. described the synthesis of stable phosphinosilylcarbenes, which can be formulated both as λ^3-phosphinocarbenes or as λ^5-phosphaacetylenes.[387a–c] *Ab initio* calculations on the parent compound suggest that the electronic structure is properly described as λ^5-phosphaacetylene, although there are some low lying triplet carbene states.[387d] Thus, this class of compounds will not be discussed further in this review.

IV. Reactions of Carbenes in Matrices

Matrix isolation spectroscopy is frequently used for the direct observation of reactions and in some cases for the determination of kinetic data. An excellent review on reactions of triplet carbenes in low-temperature glasses and solids—with emphasis on ESR spectroscopy as the analytical tool—was presented by Platz in 1990.[8] Here, a summary of classes of carbene reactions in matrices (emphasis on inert gas matrices) is given, only, while special carbene reactions are treated in the chapters of individual carbenes.

A difficulty inherent to solid-state conditions is that generally a distribution of species in matrix sites with slightly differing spectroscopic as well as kinetic properties is formed, which results in a distribution of rate constants. This is reflected in nonexponential kinetics of first and pseudo-first-order reactions which makes it difficult—if not impossible—to extract meaningful reaction rates from kinetic data. "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" and "the chemistry of singlet...[carbene]...may be entirely predestined by the local matrix site."[388a] This excerpt from a 1983 publication by Tomioka, Platz, and co-workers on the solid-state chemistry of 1,2-diphenylpropylidene[388b]—which was already cited by Chapman et al.[57]—illustrates well the difficulties which have to be faced when solution conditions no longer apply. Despite many attempts to deduce reliable information from this kind of disturbed kinetics[10,389–391] the data should be treated with great care. For bimolecular reactions—where diffusion of the reactants in the solid state is important—it is generally impossible to obtain reliable kinetic data.

A. Intramolecular Reactions

Some theoretical investigations of carbene rearrangements involving carbon or hydrogen migration have been published. These include a few *ab initio* studies,[52,380,392,393] and a larger number of semiempirical and qualitative investigations.[394–400] For further references see Evanseck and Houk.[52,380]

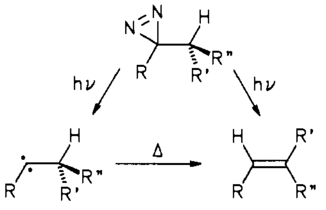
1. Hydrogen Shifts

Alkylcarbenes bearing α-hydrogens undergo rapid thermal 1,2-[H]-shift to yield the corresponding olefins. At ambient temperature in dilute solution, this reaction determines the lifetime of these carbenes in many cases. Typical rate constants are in the range of 10^6 to 10^8 s^{-1}, with activation energies of about 1–5 kcal/mol and relatively low pre-exponential factors of 10^8–10^{11} s^{-1}.[401,402]

Although precursor photolysis in matrix isolation experiments takes place at temperatures as low as 4–10 K, direct observation of the thermal rearrangement is often difficult to achieve due to the relatively low time resolution of these experiments (minutes) and the possibility of thermally excited "hot" carbenes to rearrange during precursor photolysis and/or rearrangements from excited states of the precursor.

The first thoroughly conducted kinetic analysis of intramolecular hydrogen shift reactions of ground-state triplet carbenes in matrices (the *o*-tolylcarbene to *o*-xylylene 1,4-[H]-shift and the phenylmethylcarbene to styrene 1,2-[H]-shift) was published by McMahon and Chapman in 1987.[57] Matrix isolation of benzylchlorocarbene (**202**) allowed the observation of the thermal hydrogen shift of a ground state singlet carbene.[59] While phenylmethylcarbene (**56**) (triplet ground state) was found to be stable at 10 K, **202** (singlet ground state) was not, which might indicate the influence of the spin state on carbene rearrangements.

In a number of cases the carbene could not be detected, i.e. only the hydrogen rearrangement products were present in the matrix after photolysis of the precursor. This was the case after decomposition of 1-(4-methoxyphenyl)diazoethane[57] and 8-methyl-1-naphthyldiazomethane,[129-131,133] where the H-shift leads to a biradical. In these cases the intermediacy of the carbene could not be established by matrix spectroscopy. Most probably, there is a pathway from an excited state of the precursor directly to the olefin.



2. Migration of Alkyl and Aryl Groups

Although the rigidity of a matrix environment hinders migration of larger groups and thermal rearrangements of this kind could not be observed so far, photochemical carbon shifts are frequent. Photolysis of carbene precursors often results in the formation of rearranged products (see above). It was shown that phenyl migration during photolysis of 1,2-diphenyl-1-diazopropane becomes predominant over concurrent H-migration when the reaction temperature is lowered, but is almost completely eliminated in the solid state.[388] No phenyl migration at all was observed after photolysis of benzylchlorodiazirines, which are precursors of singlet carbenes, and it was concluded that phenyl migration is a reaction of the triplet state.[403]

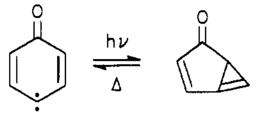
3. Other Rearrangements

Important carbene rearrangements that have been investigated in matrices are the Wolff rearrangement, the ring expansion of phenylcarbenes to cycloheptatetraenes, and the vinylcarbene–cyclopropene rearrangement.

The Wolff rearrangement (Scheme III) has synthetic as well as technical applications and therefore was target of several studies (see section B). Although the kinetics of disappearance of α-ketocarbenes was reported several times, data obtained by ESR are not very reliable, because the formation of diamagnetic products can principally not be observed. Thus it is not possible to discriminate between rearrangement and intermolecular pathways (dimerization, reaction with the organic glass, etc.). IR spectroscopy is the method of choice to observe both the carbenes disappearing and the newly formed ketenes growing in. The only ketocarbenes that have been characterized by IR spectroscopy were Chapman's carbenes **120**–**122**[207,208] and Tomioka's carbene **123**.[209] Unfortunately, no thermal rearrangement was observed in these cases, and therefore no kinetic data could be obtained.

The photochemical ring enlargement of phenylcarbenes to cycloheptatetraenes has been studied by Chapman et al.[72,76,279-281] and is described in sections III.A.3 and III.C.5 (Scheme IX). Under FVP conditions phenylcarbenes thermally rearrange and cycloheptatetraenes are trapped, but the barriers toward rearrangement are high enough to prevent thermal rearrangement in inert gas matrices at low temperatures, and thus kinetic studies could not be conducted.

The kinetics of a cyclopropene–vinylcarbene rearrangement has been studied by our group.[269,270] A curved Arrhenius plot was observed, and at temperatures below approximately 20 K the rates of this rearrangement became independent of temperature.[269] This was taken as evidence for a quantum mechanical tunneling mechanism (heavy-atom tunneling). Evaluation of the kinetic data using a modified Arrhenius equation according to Bell[404] gave an activation barrier in the order of 2.5 kcal/mol (depending on the matrix) and a tunneling distance of 0.4 Å under the assumption of a mass of 12 (carbon atom) tunneling. At 10 K the rates of rearrangement depend much on the matrix and in Kr are 5 times and in Xe 37 times faster than in Ar. Together with the observed very small Arrhenius preexponential factors A this observation suggests that the rate-determining step of the rearrangement involves the ISC and the singlet cyclopropene directly rearranges to the triplet carbene in a formaly spin-forbidden reaction.



B. Intermolecular Reactions

1. Atom Abstractions and Insertion Reactions

Intermolecular atom abstraction to produce radical pairs is one of the most important reactions of triplet carbenes, and H atom transfer is the dominant decay process of carbenes in organic glasses.[289,388a] H- and Cl-abstractions have been extensively studied by ESR spectroscopy and reviewed by Platz several times,[8,10] and therefore only a brief summary will be given here.

Pseudo-first-order Arrhenius parameters for diphenylcarbene (**17**) in a variety of organic glasses (e.g. benzene, toluene, cyclohexene, and the deuterated counterparts) were reported. ESR signals were produced by brief photolysis of diphenyldiazomethane, and the decay of signal intensity is followed immediately afterward.[10] E_a varied between 2.1 (toluene) and 3.2 kcal/mol (cyclohexene), the Arrhenius preexponential factor A was very small (log A between 2.1 and 4.3), and a pronounced kinetic deuterium isotope effect was observed.[405,406] On the basis of these experiments, quantum mechanical tunneling (QMT) was proposed as mechanism for H-abstraction. This was supported by the observation that **17** was completely stable in carbon tetrachloride at 77–100 K, which implies that chlorine, in contrast to hydrogen, is not abstracted by a QMT mechanism.[407] Similar observations were reported for other triplet carbenes such as fluorenylidene (**136**) or dibenzocycloheptatrienylidene (**179**).[10,407] Platz et al. were able to measure both the decay of the triplet signal intensity of **136** and dibenzocycloheptadienylidene **181** in organic glasses at 77 K as well as the formation of triplet radical pairs as primary products of the H transfer.[289]

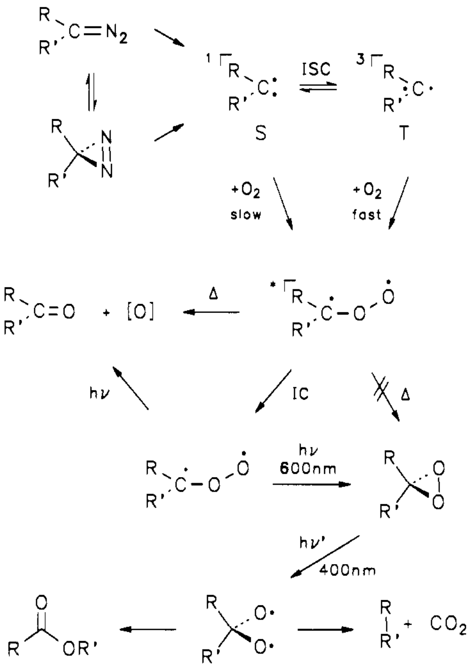
One problem with experiments in organic glasses is secondary photolysis, if the photochemical generation of carbenes and subsequent thermal reactions are not rigorously separated.[408] Many carbenes are long-lived enough even in reactive matrices such as frozen alcohols to become electronically excited during photolysis of the precursor. Electronically excited carbenes are expected to exhibit a very different chemical behavior compared to the ground-state carbenes. Thus triplet diphenylcarbene (**17**), generated by irradiation of diphenyldiazomethane in frozen alcohols at 77 K, produces mainly ethers, the products of formal OH-insertion, in a thermal reactions. Alcohols, the products of the formal CH-insertion, are photoproducts rather than thermal products.[408] It was also shown that triplet fluorenylidene (**136**) is less sensitive to secondary photolysis.

In doped inert gas matrices with an excess of inert gas (200:1 to 10:1 excess) the generation of the carbene is in most cases separated from the thermal intermolecular reaction by a diffusion step. This allows one to first characterize the carbene in its ground state at temperatures below 12 K, and then induce the thermal reaction by annealing the matrix above 20–30 K. Typical ratios of carbene/reagent/inert gas are 1:10:1000. So far, H-abstractions in doped inert gas matrices have not been reported, but intermolecular reactions of carbenes with small molecules are frequently investigated in this type of matrix.

2. Reactions with Oxygen

The oxidation of carbenes with molecular oxygen is now fairly well understood and frequently used to identify matrix-isolated carbenes.[28,409] Both singlet and triplet carbenes give carbonyl *O*-oxides (Criegee intermediates) as primary adducts upon annealing (30–40 K) of O_2-doped inert gas matrices. Carbonyl oxides are easily identified by their strong $\pi \rightarrow \pi^*$ absorption in the visible region (in most cases the matrix turns intense yellow to red) and by their intense O–O stretching vibration around 900 to 1000 cm^{-1}.[28] Carbonyl oxides are extremely photolabile and irradiation with red light (600 nm) rapidly produces dioxiranes (Scheme XIV). The dioxiranes are stable under these conditions but at 400-nm irradiation are converted to esters or lactones. In several cases CO_2 was observed as a byproduct of this photochemistry. The sequence carbonyl oxide–dioxirane–ester is easily followed spectroscopically and highly characteristic for matrix-isolated carbenes in O_2-doped matrices. Singlet carbenes such as phenylchlorocarbene (**193**) are oxidized several orders of magnitude more slowly than triplet carbenes. The same difference in reactivity was also observed in solution at room temperature using LFP and nanosecond time resolution.[410] The more electron-deficient (*p*-nitrophenyl)chlorocarbene (**198**) reacts markedly faster both in matrix[366] and in solution,[410] indicating an electrophilic attack of the carbene on the O_2 molecule.

Scheme XIV



An interesting observation reported first by Wasserman et al. was the emission of a strong chemiluminescence during warmup of organic glasses containing diphenylcarbene (**17**)[68] or bis(trifluoromethyl)carbene (**7**)[63] and traces of oxygen. The mechanism leading to chemiluminescence was later investigated by Turro et al.[139] Following the carbene concentration in O_2-doped freon glasses at temperatures >77 K by ESR and fluorescence spectroscopy, and simultaneously measuring the chemiluminescence spectra and intensity, revealed that chemiluminescence decay was faster than consumption of the carbenes. In all cases the chemiluminescence was identified as phosphorescence of the corresponding carbonyl compounds. From these experiments oxygen transfer from carbonyl oxides to carbenes, leading to carbonyl compounds in electronically excited states, was proposed as the step leading to emission of light.

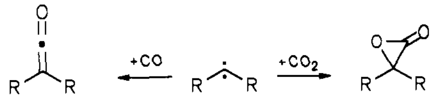
In a similar experimental setup we could show that in O_2-doped Ar matrices chemiluminescence starts at temperatures as low as 15 K.[73,74,79,411] Again, chemiluminescence decay was faster than oxidation of the carbenes, but IR spectroscopy excluded carbonyl oxides as oxygen-transfer reagents. The direct reaction of oxygen atoms (produced by decomposition of carbonyl oxides) with carbenes, producing a C=O bond in situ in a very exothermic reaction, was now proposed as chemiluminescent step (Scheme XIV).

3. Other Intermolecular Reactions

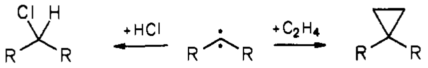
Dimerization of carbenes is an important reaction in solution, but in matrices due to the slow diffusion of larger molecules it is only rarely observed. The dimerization of methylene was reported by Milligan and Pimentel (Scheme I).[1] Other dimerizations which have been observed directly are that of cyclopentadienylidene (**133**),[29,228,412] methoxycarbenes **208**[413] and **212**,[381] and of bis(trifluoromethyl)carbene (**7**, Scheme II).[64]

The carbonylation of carbenes produces ketenes, which are easily identified by IR spectroscopy. This reaction is generally slower than the oxidation with O_2, and higher concentrations of CO (2–5%) than O_2 (<2%) are required to get comparable yields of products on annealing the matrices. In most cases the appearance of a new IR absorption in the range 2000–2200 cm^{-1} is taken as evidence for the formation of a ketene. As long as the ketene has not been identified by direct comparison with the authentic matrix isolated ketene, this has to be taken with some caution. Several triplet carbenes were characterized by CO trapping: methylene,[2] methylcarbene (**1**),[53] 3-pyridylcarbene (**53**),[136] bis(trifluoromethyl)carbene (**7**),[64] cyclopentadienylidene (**133**) and derivatives,[29,234] 4-oxo-2,5-cyclohexadienylidene (**158**),[264] and cycloheptatrienylidene (**169**). (See discussion in section III.C.5 about the identification of this carbene.[282])

The formally spin-allowed carbonylation of singlet carbenes should be faster, but so far dicyclopropylcarbene (**3**) is the only singlet carbene that has been trapped with CO.[56]



Carboxylation of carbenes leads to α-lactones (oxiranones), which are not easily accessible by other methods. The parent α-lactone was produced by irradiation of diazomethane in solid CO_2 at 53 K (Scheme I).[45] Comparison of the rates of carboxylation of diphenylcarbene (**17**), phenylchlorocarbene (**193**, Scheme XII), and (*p*-nitrophenyl)chlorocarbene (**198**) revealed that this reaction is not governed by the spin multiplicity, but rather by the philicity of the carbene, and nucleophilic attack of the carbene at the CO_2 carbon atom is rate determining.[366]



HCl trapping is frequently used to provide chemical evidence for the formation of singlet carbenes in matrices.[58,365,376] The chlorides formed are generally stable molecules which can be matrix isolated independently to compare the spectra. Kinetic data relating to this reaction have not been reported.

The direct observation of the reaction of a carbene and ethylene was reported by Mal'tsev et al.[233,412] Annealing of a 2% ethylene-doped argon matrix containing cyclopentadienylidene (**133**) at 40–45 K produced [2.4]spiro-4,6-heptadiene.

V. Conclusions

Matrix isolation spectroscopy is now a well-established technique for the determination of spectroscopic as well as chemical properties of carbenes. Numerous carbenes are completely stable under these conditions—especially in inert gas matrices—and can be characterized with routine spectrometers available in most laboratories. Although a wealth of spectroscopic data of more than 200 carbenes has been published during the years, due to the limited number of spectroscopic methods applicable to solid-state matrices, important information is still lacking. Structures of carbenes have been deduced from ESR data. The information obtained by this method is limited basically to the bond angle at the carbene center, it has to be taken with some care, and is not available for singlet carbenes. Thus, the determination of structural data of carbenes is a rewarding goal for future research. A practical approach to this might be the use of oriented matrices using photoselection or solid-state NMR techniques. Another field which is still underdeveloped is the direct observation of reactions in matrices. Some reactions like the oxidation with molecular oxygen are now frequently used, but the number of reactions which could lead to new and fascinating molecules and provide insight into details of mechanisms which are not available by other methods is almost only limited by imagination.

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