Translated from *Uspekhi Khimii* **58** 1091–1104 (1989) U.D.C. 543.422.4:541.144.8

Spectroscopic study of carbenes in low-temperature matrices

P S Zuev, O M Nefedov
Zelinskii Institute of Organic Chemistry, USSR Academy of Sciences, Moscow

ABSTRACT. The review surveys and gives a systematic account of the literature data on the IR and UV spectroscopic studies on carbenes in low-temperature matrices. The methods of generation and isolation of carbenes in inert matrices at temperatures around 10 K are examined. The possibility of applying the data obtained to the study of the structure of carbenes and to the determination of the mechanisms of reactions involving them is demonstrated.

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I. Introduction

In connection with the wide-scale application of reactions involving carbenes in synthetic organic chemistry, there has been a sharp growth of interest during the last 15–20 years in the detailed investigation of these species by various physicochemical methods. Such studies not only make it possible to detect and identify carbenes but also provide information about their structure, which is important for the interpretation of the reaction mechanisms.

The principal difficulties in the direct spectroscopic detection of carbenes (as well as other unstable molecules) are associated with the high reactivity and the short lifetime of these species under normal conditions. There are two ways of overcoming these difficulties. The first is based on the use of pulse methods in order to create a high concentration of the unstable compounds during a short time interval (10^{-3} s and less). In this case the spectroscopic characteristics of the test species can be obtained with the aid of special high-speed devices. Another, more widely used method consists in the isolation of the unstable intermediates in low-temperature matrices, primarily in inert gas matrices at temperatures below 20 K (the matrix isolation method), which makes it possible to prevent secondary reactions and to increase almost indefinitely the lifetime of these species. The methods for the generation of carbenes in low-temperature matrices will be examined in greater detail below. The application of the matrix isolation method in combination with analytical procedures such as EPR, UV, and IR spectroscopy has proved extremely fruitful.

This review discusses the results of IR and UV spectroscopic studies on carbenes in low-temperature matrices obtained during the last 10 years. Earlier investigations have been surveyed in other publications.[1,2] Nor do we examine matrix studies using EPR, since they have been surveyed fairly completely in other reviews.[3–5]

II. Methods for the generation of carbenes in low-temperature matrices

Various methods are used to generate carbene in matrix studies. They can be obtained in the gas phase under the influence of a high temperature or a discharge (electrical, microwave, or radio-frequency) with subsequent freezing of the species formed in a low-temperature matrix. These methods have been examined in another review[6] and here we shall not deal with them in detail. We shall only note that the simplest triatomic carbenes can be isolated from the gas phase. More complex carbenes have sufficient time to undergo secondary reactions during their time of flight from the reactor to the cooled zone.

The most widely used method of synthesis of complex carbenes (i.e. carbenes consisting of more than three atoms) involves their generation by the UV photolysis of precursor molecules, mainly diazo-compounds and diazirines, isolated in inert matrices. The advantage of this method consists in the simplicity of the preparation of the matrix containing the stable initial compound, which is subsequently decomposed directly in the isolated state. The photodissociation of diazo-compounds and diazirines, yields, apart from the corresponding carbenes, also nitrogen molecules which are fairly inert and do not normally enter into recombination reactions with carbene molecules within the matrix cage. The majority of carbenes dealt with in the present review have been obtained by this method. Among other methods for the generation of carbenes in a low-temperature matrix, mention should be made of the reactions of stable molecules with free atoms, in particular with alkali metal atoms. The results of these investigations have been discussed in other reviews.[2,6]

III. IR and UV spectroscopic study of carbenes and their reactions

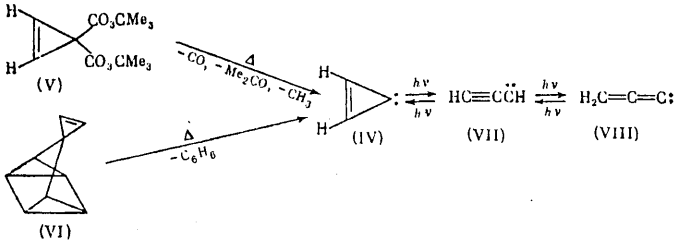
The comparatively small size of the simplest carbene (methylene) ensures that it has a definite mobility even in frozen inert matrices, which leads to the formation of dimerisation products under these conditions. It was not until 1981 that it became possible to detect[7] in the spectra of the diazomethane photolysis products bands at 1015 cm^{-1} (Ar matrix) and 1109 cm^{-1} (Xe matrix), which were attributed to the deformation vibration of methylene in its ground triplet state.

Dichlorocarbene (III) was formed on UV photolysis of dichloroketen (I), obtained by the thermal reaction of trichloroacetic acid chloride (II) with zinc and frozen in an Ar matrix at 12 K.[8]

The recombination of the carbene (III) with a CO molecule in the matrix cage was not observed:

$$\underset{\text{(II)}}{CCl_3\overset{O}{\overset{\|}{C}}Cl} \xrightarrow[-ZnCl_2]{\Delta,\,Zn} \underset{\text{(I)}}{Cl_2C{=}C{=}O} \xrightarrow[-CO]{h\nu(\lambda>200\text{ nm})} \underset{\text{(III)}}{Cl_2C:}\,.$$

Cyclopropenylidene (IV) has been obtained from two different sources — compounds (V) and (VI) — by their thermal decomposition in the gas phase.[9,10] The subsequent UV photolysis (λ = 313 and 254 nm) of this carbene in an Ar matrix led to its isomerisation to propargylene (VII) and further to vinylidenecarbene (VIII). The vibration frequencies of the carbene (VIII) were calculated from its matrix IR spectrum and it was shown that it has a singlet ground state. The results agree well with data obtained by the EPR method.[10]



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$$\underset{\text{(X)}}{N\equiv C\overset{N_2}{\overset{\|}{C}}H} \xrightarrow[-N_2]{h\nu} \underset{\text{(IX)}}{N\equiv C\ddot{C}H}.$$

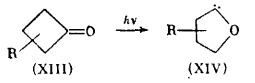
Taking into account the linear structure of the carbene (IX),[11] Dendramis and co-workers[12,13] carried out a full vibrational analysis of the spectra obtained and determined the force field of this species. Analysis of the numerical values of the valence force constants of the CC and CN bonds showed that their multiplicity in both cases is close to two. This as well as the high constant for the interaction of the CC and CN bonds indicate a high degree of delocalisation of electrons in the carbene (IX) and the similarity of its structure to the allene structure $\dot{N}{=}C{=}\dot{C}H$). The UV absorption spectrum of the cyanocarbene (IX) consists of a progression of bands in the range 240–340 nm. Estimation of the energy differences between the members of this progression makes it possible to assign it to the symmetrical stretching vibrations of the N=C=C group of the carbene in the electronically excited state.

The IR spectrum of dicyanocarbene has been obtained and its vibrational spectrum has been calculated.[13]

The IR spectrum of bis(trifluoromethyl)carbene (XI), generated by the UV photolysis (λ > 200 nm) of bis(trifluoromethyl)diazirine (XII), isolated in an Ar matrix at 12 K, has been published.[14,15] In contrast to the photodecomposition of the diazirine (XII), in the low-temperature matrix its gas-phase pyrolysis (300–500 °C) in the absence of the molecular collisions in the thermal reaction zone did not lead to the appearance of the carbene (XI) band in the matrix IR spectrum of the product. The only product of the thermal reaction was perfluoropropene—an isomer of the carbene (XI). The time taken for the rearrangement of the carbene (XI) in the excited singlet state to perfluoropropene has been estaimted[14,15] to be approximately 10^{-5} s:

$$\underset{\text{(XII)}}{(CF_3)_2C\overset{N}{\underset{N}{\diagup\!\diagdown}}} \xrightarrow[-N_2]{\Delta} \underset{\text{(XI)}}{[(CF_3)_2C:]^S} \rightarrow CF_3CF{=}CF_2.$$

Quantum-chemical calculations have shown that oxycarbenes have a singlet ground state,[16,17] which is stabilised by the interaction of the unshared electron pair of the oxygen atom with the unoccupied *p* orbital of the carbene centre. As a result of this, it is impossible to detect such species by EPR, which makes spectroscopic data obtained by other methods especially valuable. However, until recently the only successful example of this kind was a study[18] in which thermally unstable species with an absorption maximum in the electronic spectrum near 360 nm were detected on UV photolysis (λ > 300 nm) of a series of cyclobutanones (XIII) in organic glasses at 77 K. This absorption was attributed to tetrahydrofurylidene (XIV)—an oxycarbene formed from cyclobutanone as a result of photolytic rearrangement with ring expansion:

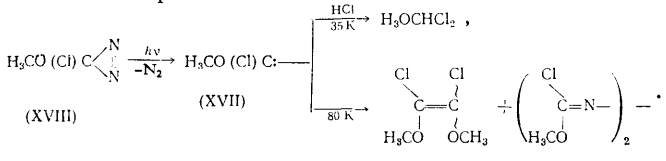


According to Quinkert et al.,[18] the carbenes (XIV) can be "captured" by alcohols, alkenes, or oxygen with formation of secondary products of the kind usual in such cases.

The attempt to measure the IR spectrum of the hydroxycarbene (XV) on UV photolysis (λ > 220 nm) of the formaldehyde (XVI) in an Ar matrix[19,20] was unsuccessful despite the fact that the structure of the final products of the reactions occurring suggest the intermediate participation of the carbene (XV) in the process. The carbene (XV) is probably sufficiently mobile even in a rigid matrix to be able to diffuse from the matrix cage and enter into the reaction:

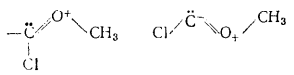
$$\underset{\text{(XVI)}}{H_2CO} \xrightarrow{h\nu} [H_2CO]^* \rightarrow \underset{\text{(XV)}}{[HO\ddot{C}H]} \xrightarrow{H_2CO} H_2C(OH)CHO.$$

Quite recently it has been possible[21,22] to record the IR and UV spectra of chloromethoxycarbene $H_3CO\ddot{C}Cl$ (XVII) and its isotope-substituted analogues $D_3CO\ddot{C}Cl$ and $H_3C^{18}O\ddot{C}Cl$, which were obtained by the UV photolysis (λ > 340 nm) of the corresponding diazirines (XVIII) isolated in matrices (Ar and N_2 12 K, 3-methylpentane, 45 K). At the same time the structure was confirmed by carrying out reactions with HCl and the initial diazirine as well as the dimerisation reaction, which occurs when the matrix is heated to the diffusion temperature:



According to Kasselmayer and Sheridan,[22] the unusually high stretching vibration frequency of the CO bond in the IR spectrum of chloromethoxycarbene (1300 cm^{-1}) is a consequence of an appreciable increase in the multiplicity of the carbon–oxygen bond as a result of the interaction of the unshared electron pairs of the oxygen atom with the unoccupied *p* orbital of the carbene centre.

The increased multiplicity of this bond suggests the possible existence of two isomeric forms of the carbene (XVII):

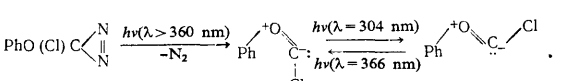


cis-(XVII) *trans*-(XVII).

Analysis of the IR spectra of the carbene (XVII) in different matrices as well as the results of experiments involving its prolonged irradiation with UV light at different wavelengths made it possible to discover the frequencies characteristic of each isomer. For example, the bands at 1310 and 1300 cm^{-1} were assigned to the antisymmetric stretching vibration of the CO bond in the *trans*- and *cis*-isomers respectively (the small frequency difference agrees with calculations of the vibrational spectra of hydroxycarbene[23]). The somewhat greater difference between the vibrational frequencies of the C–Cl bond in the *trans*- and *cis*-isomers of the carbene (XVII) (780 and 755 cm^{-1} respectively) is probably induced by the delocalisation of the unshared electron pair of the oxygen atom over the non-bonding σ orbital of the C–Cl bond.[24] The UV spectrum of the carbene (XVII) isolated in a N_2 matrix contains an absorption band in the region of 360 nm (the authors[22] were unable to differentiate the absorption bands due to different isomers). The extinction coefficient of the carbene was estimated approximately as 65 mol $litre^{-1}$ cm^{-1}.

Prolonged irradiation of the carbene (XVII) in a Ar matrix with UV light (λ > 270 nm) leads to its rearrangement to acetyl chloride, which partly decomposes with formation of keten and hydrogen chloride. The irradiation of compound (XVII) in a N_2 matrix induces the formation, apart from the products indicated, also of small amounts of methyl chloride and CO. The mechanisms of the reactions occurring have not been fully elucidated.

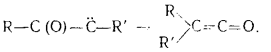
In the course of continuing studies on substituted oxycarbenes, the matrix IR and UV spectra of another representative of unstable species of this class—chloro(phenoxy)carbene (XIX)—were recorded.[25] Groups of bands due to the *cis*- and *trans*-isomers, which can be interconverted on irradiation with UV light at definite wavelengths, were differentiated in the IR spectra of both compound (XIX) and (XVII):



cis-(XIX) *trans*-(XIX)

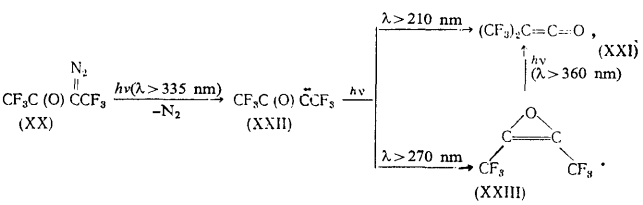
The higher frequency of the antisymmetric stretching vibrations of the CO bond in both isomers confirms, as in the previous case, its increased multiplicity. The bands at 850 cm^{-1} [*trans*-(XIX)] and 800 cm^{-1} [*cis*-(XIX)] have been assigned to the C–Cl bond stretching vibrations. The authors do not comment on the similar somewhat high C–Cl vibration frequency,[25] although by analogy with the carbene (XVII) one would be justified in expecting frequencies in the range 750–780 cm^{-1}. The UV spectrum of the carbene (XIX) has a broad absorption band with λ = 320 nm whose extinction coefficient has been estimated as 100 cm^{-1} mol^{-1}. Compound (XIX) behaves photochemically similarly to the carbene (XVII): the prolonged photolysis of the carbene (XIX) isolated in a N_2 matrix leads to the formation of benzoyl chloride, chlorobenzene, and CO.

For a long time, the spectroscopic data for carbonylcarbenes of the type R–C(O)–C̈–R′ were restricted to EPR spectra.[26–29] The attainment of higher concentrations of these carbenes, sufficient for their detection in matrices by IR and UV spectroscopy, is prevented by the ease with which they rearrange to the isomeric ketens[30,31] (the Wolff rearrangement):



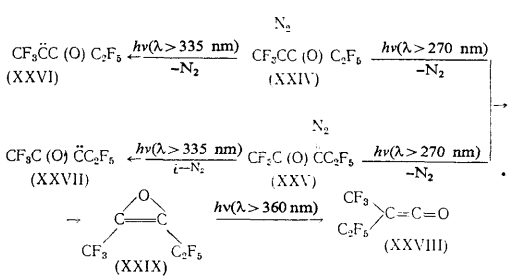
The rearrangement can be slowed down by stabilising the carbenes by introducing an electron-accepting substituent at the carbene centre and also by increasing the size of the migrating group. The first procedure is more effective, because an increase in the size of the substituent can lead to intramolecular secondary reactions in the carbene (for example, intramolecular insertion in the CH bond[32]).

Torres et al.[33] investigated the UV photolysis (λ > 335 nm) of hexafluoro-3-diazo-2-butanone (XX) in an Ar matrix. Together with bis(trifluoromethyl)keten (XXI), the carbene (XXII), which on subsequent irradiation (λ > 210 nm) was converted into the keten (XXI), was detected in the photolysis products by IR spectroscopy:



On the other hand, the irradiation of the carbene (XXII) by light at a longer wavelength (λ > 270 nm) leads to the appearance in the IR spectrum of bands due to a new unstable species, which is also converted into ketens on prolonged irradiation. The appearance of these new bands was explained by the formation of bis(trifluoromethyl)oxirene (XXIII) in the matrix. The intermediate formation of oxirenes has been postulated in a number of reactions,[34–36] but previously they could not be detected spectroscopically. Theoretical calculations have shown that oxirenes are thermodynamically less stable than the isomeric carbonylcarbenes.[37]

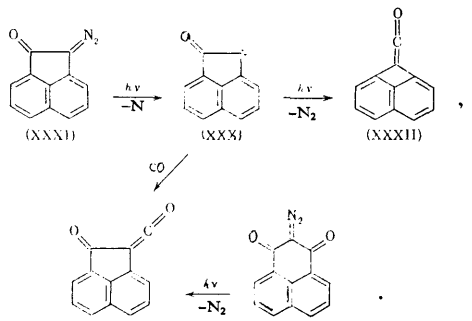
In order to confirm the conclusion that the oxirene (XXIII) is formed, a study was made[33] of the UV photolysis of two other perfluorodiazoketones—2-diazo-octafluoro-3-pentanone (XXIV) and 3-diazo-octafluoro-2-pentanone (XXV)—in an Ar matrix at 12 K:



Apart from the bands of the corresponding carbenes (XXVI) and (XXVII), the bands of only one unstable species were detected in the IR spectra of the products of the photolysis of compounds (XXIV) and (XXV) by UV light at λ > 270 nm. The conversion of this species into the keten (XXVIII) on further irradiation confirms its oxirene structure (XXIX).

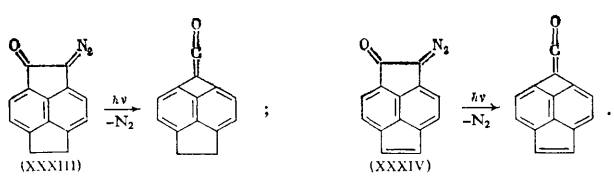
The IR and UV spectra of α-ketocarbene (XXX) were obtained on UV photolysis by light at λ = 365 ± 8 nm of the diazo-compound (XXXI) isolated in an Ar matrix at 10 K. The

formation of the carbene (XXX) was confirmed by the reactions with O_2 and CO:

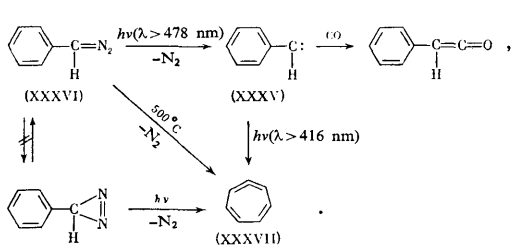


Further irradiation of the carbene (XXX) (λ = 625 ± 8 nm) leads to the Wolff rearrangement and the formation of the keten (XXXII).

In contrast to the example examined above, the attempts to generate ketocarbenes with similar structures by the matrix photolysis of the diazo-compounds (XXXIII) and (XXXIV) were unsuccessful: in both cases, the only detectable products of the photolytic reaction were the corresponding ketens obtained as a result of the Wolff rearrangement (XXXVIII).

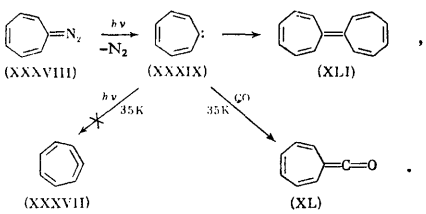


The IR and UV spectra of phenylcarbene (XXXV), formed on UV photolysis (λ > 478 nm) of phenyldiazomethane (XXXVI) in an Ar matrix, have been recorded.[39] Prolonged irradiation of the matrix-isolated carbene (XXXV) by UV light at a shorter wavelength (λ > 416 nm) leads to the disappearance from the IR spectrum of the absorption band characteristic of the aromatic ring and the methylidyne group and to the appearance of IR bands of an unknown compound. The same compound was detected among the products of the gas-phase pyrolysis of phenyldiazomethane (XXXVI) (500 °C), frozen in the matrix, and also on matrix photolysis of phenyldiazirine. The presence in its spectrum of bands at 1824 and 1816 cm^{-1}, close to the 1810 cm^{-1} band characteristic of the allene linkage of 1-azocyclohepta-1,3,4,6-tetraene,[40] indicates the formation of the cycloheptatetraene (XXXVII)—the product of the intramolecular reaction of the carbene (XXXV) with ring expansion. Analysis of the products of the matrix UV photolysis of various deuteriated phenylcarbenes has confirmed the proposed mechanism:



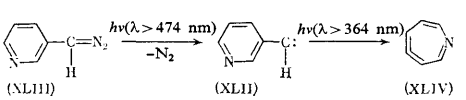
Systematic matrix studies of this rearrangement have shown that isomerisation with ring expansion and the formation of cycloheptatetraenes is a widely occurring reaction of many arylcarbenes.[41,42] The dimerisation reaction of the cycloheptatetraene (XXXVII) has also been investigated by matrix IR spectroscopy and it has been possible to discover alternative sources of this interesting cyclic compound.[42]

The IR and UV spectra of the triplet cycloheptatrienylidene (XXXIX) have been recorded quite recently[43] after the UV photolysis (λ > 574 nm) of diazocycloheptatriene (XXXVIII) in an Ar matrix. This carbene interacts with the CO added to the matrix, forming the keten (XL), and also dimerised with formation of heptafulvalene (XLI):

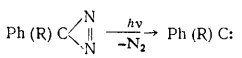


Experiments have shown that this cannot be converted into the cycloheptatriene (XXXVII) either thermally or photolytically. The presence in the electronic spectrum of compound (XXXIX) of an absorption maximum in the long-wavelength region at 530 nm suggests a planar structure of this carbene, which agrees well with EPR data.[43]

According to the results of Chapman and Sheridan,[44] pyridylcarbene (XLII), whose IR spectrum has been recorded on UV irradiation (λ > 474 nm) of 3-diazomethylpyridine (XLIII) in an Ar matrix, undergoes a photolytic rearrangement similar to that of phenylcarbene (XXXV). Thus its photolysis by UV light at λ > 364 nm leads to the formation of 1-azacyclohepta-1,3,4,6-tetraene (XLIV):



The IR and UV spectra of halogeno(phenyl)carbenes PhCCl (XLVa), PhCBr (XLVb), and PhCF (XLVc), generated by the UV photolysis (λ > 300 nm) of the corresponding diazirenes (XLVI) in inert gas matrices at 10 K[42,45–47] or in a 3-methylpentane matrix at 77 K,[48] have been described in the literature. A correspondence was observed between the electronic spectra of the carbenes (XLVa)–(XLVc), formed in a 3-methylpentane matrix, and the spectra obtained on flash photolysis of the diazirines (XLVIa)–(XLVIc) in gaseous benzene or isooctane at 23 °C:[48]



(XLVI) (XLV)

R = Cl (a), Br (b), F (c), CF_3 (d).

Phenyltrifluoromethylcarbene (XLVd), whose IR spectrum has also been recorded, has been obtained similarly by the UV photolysis of phenyltrifluoromethyldiazirine (XLVId) and phenyltrifluoromethyldiazomethane, both frozen in an Ar matrix.[47]

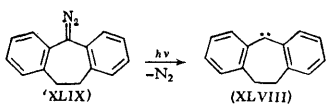
The electronic absorption and emission spectra of diphenylcarbenes (XLVII) have been obtained in the photolysis of diphenyldiazomethane isolated at 20–77 K in various crystals and vitreous organic matrices.[49–54] The spectrum of this carbene is characterised by the presence of two structureless broad bands with maxima at 301 nm (ε = 25000) and 465 nm (ε = 300) and possibly a third band at 240 nm.[51] The assignment of the observed bands to compound (XLVII) was based on their disappearance when the

matrix was heated and on the appearance of the absorption of benzophenone (in the presence of oxygen), on the parallel decrease in the intensities of the UV bands and the EPR signal due to the given carbene, and on the quantitative analogy with the electronic spectrum of the diphenylmethyl radical (absorption maxima at 336 and 515 nm). The absorption spectra of different 4-substituted diphenylcarbenes have a similar form with two main bands in the UV and visible regions. The electronic spectra of these carbenes have already been surveyed.[28]

Polarisation studies on the carbenes (XLVII), (XLVII)-d_{10}, and 4,4′-dichloro- and 4,4′-dibromo-diphenylcarbenes have made it possible to characterise the electronic configurations of the ground and first excited triplet states of these carbenes as $(p\pi)^1(p\sigma)^1$ and $(p\sigma)^1(\pi^*)^1$. Further investigations demonstrated the $(p\pi)^1(\pi^*)^1$ configuration of the second excited triplet state with an energy higher by 1000 cm^{-1} than that of the first excited triplet state.[52]

The IR spectrum of diphenylcarbene has been published.[55]

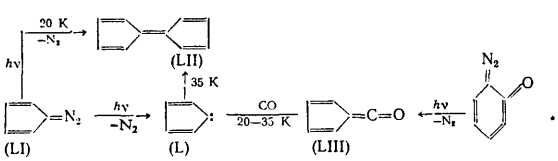
The electronic spectrum of 10,11-dihydrodibenzo[*a*,*d*]cycloheptenylidene (XLVIII) (λ_{max} = 510 nm) has been obtained in the photolysis of the corresponding diazo-compound (XLIX) frozen in various organic matrices at 77 K:[51]



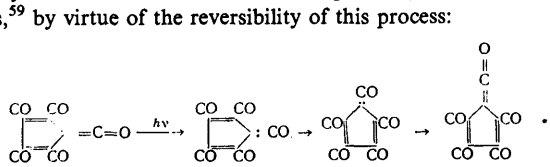
(XLIX) (XLVIII)

Later[56] the UV spectrum of this species was recorded in the flash photolysis of the diazo-compound (XLIX) in solutions in hydrocarbons at 20 °C.

After the first, partly unsuccessful (owing to the unsuccessful selection of experimental conditions) attempts to stabilise cyclopentadienylidene (L) in an inert matrix,[57,58] its IR and UV spectra were recorded.[59] The carbene (L) was obtained by the UV photolysis (λ > 300 nm) of diazocyclopentadiene (LI) isolated in low-temperature inert matrices. The reliability of the frequency assignments to compound (L) in the IR and UV spectra obtained was confirmed by the occurrence in the matrix at 20–35 K of the dimerisation of compound (L) to fulvalene (LII) and the formation of the keten (LIII) on interaction of compound (L) with the CO added to the N_2 matrix:

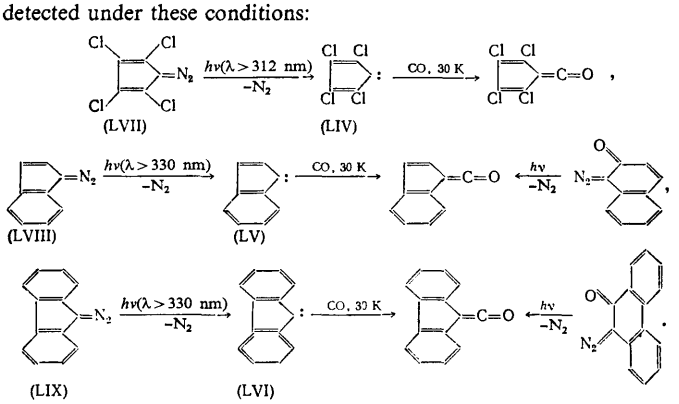


The carbene (L) is extremely reactive even at liquid helium temperature and, under the conditions of insufficient matrix dilution (less than 1000 : 1), it readily dimerises to compound (LII). Furthermore, even when the matrix dilution is raised to 100 000 : 1, a certain amount of the dimer (LII) is formed. Such high reactivity in compound (L) may be associated with its ability to rotate within the matrix cage. Photolysis by polarised light of the keten (LIII), obtained by the interaction of compound (L) with a CO molecule in a CO matrix, leads to an appreciable reorientation of the initially randomly oriented keten molecules, most probably, according to the authors,[59] by virtue of the reversibility of this process:

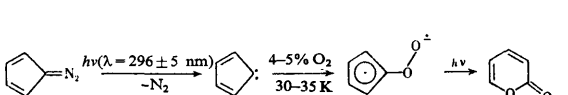


It has been possible to record[60] the IR and UV spectra of several derivatives of the carbene (L)—tetrachlorocyclopentadienylidene (LIV), indenylidene (LV), and fluorenylidene (LVI). They were all formed on UV photolysis of the corresponding diazo-precursors (LVII)–(LIX) in inert matrices and had a triplet ground state. The UV spectrum of compound (LVI), stabilised in a matrix, is close to the UV spectrum of the triplet (LVI) obtained by flash photolysis.[61] In contrast to compound (L), the dimerisation of the carbenes (LIV)–(LVI) was observed neither during their generation nor in the course of subsequent heating until the complete evaporation of the material of the matrix. According to Bell and Dunkin,[60] the possible causes of this are, firstly, the appreciably greater bulk of the carbenes considered compared with compound (L), which hinders their diffusion in the matrix and, secondly, the pronounced shielding of the carbene centres by the bulky substituents, which creates steric hindrance to dimerisation. For comparison, one should note that the formation of the dimer of the carbene (LVI) was observed only in the photolysis of diazofluorene (LVII) in solution.[62]

At 30 K in inert matrices with added CO, the carbenes (LIV)–(LVI) give rise to the corresponding ketens, although they exhibit under these conditions a lower reactivity than compound (L). Furthermore, the carbenes (LIV)–(LVI) were stabilised in a pure CO matrix at 12 K, whereas the free carbene (L) could not be detected under these conditions:



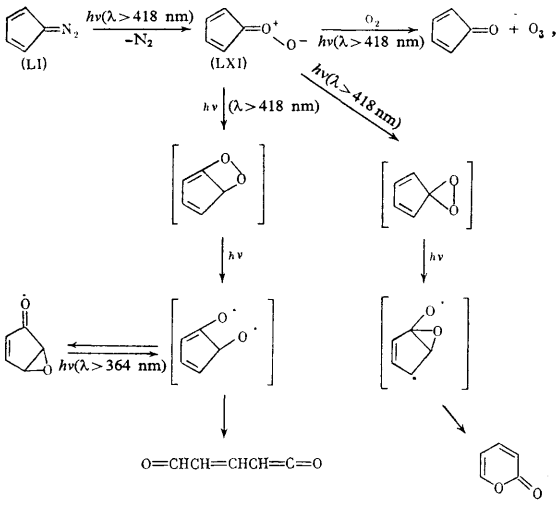
The different reactivities in relation to CO exhibited by compound (L) and its derivatives (LIV)–(LVI) may be associated, on the one hand, with the different degrees of shielding of the carbene centres and, on the other, with the different rates and hence different energies of the triplet–singlet transition of these carbenes, which necessarily precedes their reactions with singlet CO molecules.[60] The reactions of the carbenes (L) and (LIV)–(LVI) with oxygen have been investigated in a number of studies. Thus the carbene (L), generated on UV photolysis of diazocyclopentadiene (LI) in a N_2 matrix to which 4–5% of O_2 had been added, reacted with O_2 at 30–35 K, affording a new photolabile substance, which was converted on subsequent photolysis into α-pyrone:[63]



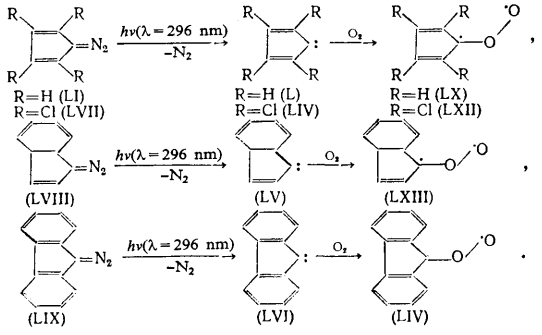
Careful analysis of the IR spectra of the compound obtained as well as examination of the isotope composition of the products formed in the presence of oxygen having the composition $^{18}O_2$ and $^{16}O^{18}O$ made it possible to attribute to this compound the structure of the oxide (LX).

Chapman and Hess,[64] who carried out the UV photolysis of compound (LI) under conditions close to those employed by Bell and Dunkin[63] (Ar matrix with addition of 25% of O_2, 10 K), also observed the formation of a photolabile product. However, the latter differed markedly from compound (LX) in terms of its set of frequencies in the IR, although the results of experiments involving the further irradiation of this compound do not conflict with the idea that it has an *O*-oxide structure [Chapman and Hess[64] postulated a zwitter-ionic structure of the carbonyl oxide (LXI) and not the radical form put forward by Bell and Dunkin[63]].

Later,[65] these discrepancies were accounted for by the fact that compound (LXI) could be formed as a result of the direct reaction of compound (LI) with O_2 without the participation of the carbene (L), especially since the usual photolytic decomposition of compound (LI) is observed on irradiation with light at a much shorter wavelength ($\lambda > 300$ nm). Furthermore, different isomers of the same carbonyl oxide may have been detected in the above studies:[63,64]

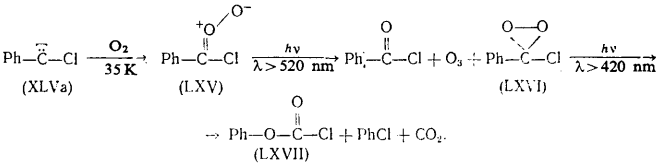


The reactions of O_2 with the carbenes (L) and (LIV)–(LVI), isolated in N_2 matrices at 10 K, were investigated by UV spectroscopy:[65]

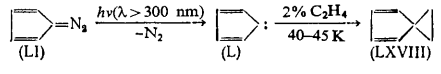


The carbonyl oxides (LX) and (LXII)–(LXIV) obtained were characterised by the presence in their electronic spectra of absorption maxima in the range 395–460 nm.

The reaction of chloro(phenyl)carbene (XLVa) with O_2 has been investigated.[45] When the Ar matrix containing 4% O_2 was heated together with the carbene (XLVa) stabilised in it from 10 to 35 K, the IR absorption of the carbene slowly weakened and new bands appeared in the spectrum, which the authors[45] assigned to the carbonyl oxide (LXV). Compound (LXV) proved to be so photolabile that it disappeared even on exposure to the IR emission from the spectrometer. The spectrum of this compound was recorded only by employing a silicon filter ($\lambda > 1100$ nm). Photolysis of compound (LXV) by light at $\lambda > 520$ nm led to its partial decomposition to benzoyl chloride and also to its rearrangement to the dioxiran (LXVI), which was converted into phenyl chloroformate (LXVII) on further irradiation. The UV spectra of compounds (LXV) and (LXVI) obtained agree well with the known spectra of the corresponding compounds of these classes:[63–65]



Finally matrix IR spectroscopy was used recently[66,67] for the direct observation and investigation of the principal reaction of carbenes—their [1 + 2]cycloaddition to alkenes—in the specific instance of the interaction of cyclopentadienylidene (L) with ethylene. UV photolysis ($\lambda > 300$ nm) of diazocyclopentadiene (LI) in an Ar matrix with added 2% C_2H_4 at 12 K resulted in the appearance in the IR spectrum of intense bands due to compound (L) together with weak bands due to its dimer (fulvalene) as well as spiro[2,4]hepta-4,6-diene (LXVIII) (734 and 560 cm^{-1}). The photolysis was continued until the complete disappearance of the bands of the initial compound (LI):



Subsequent heating of the matrix from 12 to 40–45 K resulted in a synchronous decrease in the intensity of the bands of the carbene (L) and the simultaneous intensification of the bands of the spiro-compound (LXVIII), which indicates the occurrence of the direct reaction of the carbene (L) with ethylene (Fig. 1). It must be emphasised that this is absolutely the first successful example of the direct spectroscopic investigation of the reactions of a carbene with organic acceptors.

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In conclusion we may note that the appearance in recent years of a large number of publications devoted to the direct spectroscopic study of carbenes and the examination of their reactions with trapping reagents and secondary reactions in low-temperature matrices indicates the growing importance of the matrix isolation method not only as a way of stabilising the carbenes and of

determining their analytical characteristics but also as an important instrument for the study of the mechanisms of processes in which they participate.

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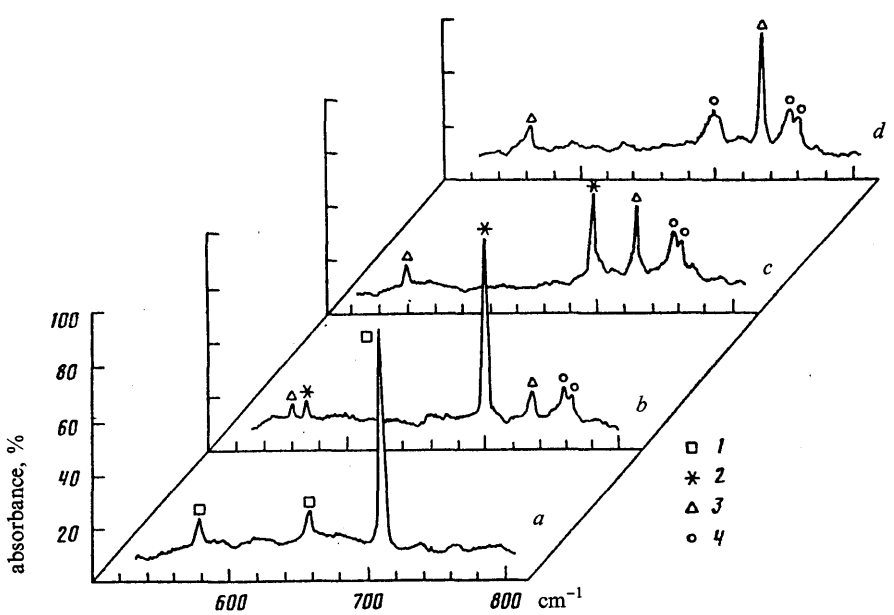


Figure 1. IR spectra of the products of the reaction of diazo-cyclopentadiene in an Ar matrix to which 2% C_2H_4 has been added: *a*, the spectrum of the initial compound before photolysis (12 K); *b*, after UV irradiation at 12 K ($\lambda > 300$ nm, 15 min); *c*, after heating the matrix from 12 to 40–45 K (10 min); *d*, ditto after intermediate recooling to 12 K; *1*, diazocyclopentadiene (LI); *2*, cyclopentadienylidene (L); *3*, spiro[2,4]hepta-4,6-diene (LXVIII); *4*, fulvalene.[66]

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