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The Electronic Structure and Reactivity of Cyclohexadienone Carbenes

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The structure, multiplicity of the electronic states, and reactivity of cyclohexadienone carbenes are discussed. The literature on the chemical behaviour of such carbenes has not previously been surveyed. Only monocylic carbenes of the above type are considered.
The bibliography includes 70 references.

CONTENTS

I. Introduction 816
II. Electronic structure of cyclohexadienone carbenes 816
III. The multiplicity of the electronic states of reacting cyclohexadienone carbenes 817
IV. Reactions of cyclohexadienone carbenes 819

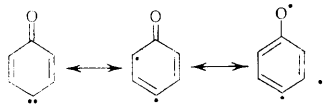
I. INTRODUCTION

Derivatives of bivalent carbon (carbenes) have continually attracted the attention of chemists in various countries. This is because of the possibility of calculating relatively easily by quantum-mechanical methods the structures of the simplest carbenes and of investigating the reactivities of these species as a function of their structure. Furthermore, a wide variety of carbenes are used extensively in preparative organic chemistry. For this reason, a series of monographs and reviews have been devoted to the chemistry of carbenes [1-9]. The chemical behaviour of cyclohexadienone carbenes differs very sharply from that of carbenes of other types. Various aspects of their structure and chemical reactions are important for theoretical organic chemistry, but have not previously been discussed in the literature.

Monocyclic carbenes of this type are used successfully in the synthesis of derivatives of sterically hindered phenols, which are inhibitors of radical processes [10]. Vigorous research is being prosecuted at the Institute of Chemical Physics of the USSR Academy of Sciences under the supervision of Academician N. M. Emanuel' on the applications of typical radical process inhibitors in various fields of experimental medicine, biology, and chemistry [11]. Sterically hindered phenols and their derivatives are employed most widely as inhibitors of the thermo-oxidative degradation of polymeric materials, oils and fuels.

II. ELECTRONIC STRUCTURE OF CYCLOHEXADIENONE CARBENES

The cyclohexadienone carbenes are a special type of cyclic carbenes whose conjugated system exhibits a very marked tendency towards the formation of an aromatic structure. Following the abstraction of the nitrogen molecule from the initial diazo-oxide†, the non-bonding electrons in the resulting cyclohexadienone carbene may be initially distributed between the σ and p_z orbitals. As in the case of cyclopentadienylidene, the electron in the p_z orbital can interact with the π-electron system of the diene. In cyclopentadienylidene this interaction leads only to the stabilisation of the triplet form without any rearrangement of the overall electronic structure of the molecule. On the other hand, in cyclohexadienone carbenes an aromatic structure is formed with an energy gain owing to conjugation (approximately 1.5 eV). The redistribution of electrons results in the formation of the carbene, which can be characterised by the following set of structures:



The distribution of non-bonding electrons is such that the σ-electron system of cyclohexadienone carbenes is to a large extent similar to that of the phenyl radical and their π-electron system is similar to that of phenoxy-radicals.

The general characteristics of the electronic structure of cyclohexadienone carbenes lead to the conclusion that their lifetime in the ground state (at any rate at low temperatures in an inert matrix) should be much longer than that of the simplest methylenes. This is confirmed by ESR data [12,13]. The ESR spectrum of unsubstituted cyclohexadienone carbene, obtained in the photolysis of benzene 1,4-diazo-oxide using filtered light in a *p*-dichlorobenzene matrix at the temperature of liquid nitrogen, consists of several signals. The most intense signal is located at zero field, while the remaining signals, with decreasing intensities, are in the region of 4550, 4770, and 6670 G. The observed signals have a very remarkable fine structure—they all exhibit distinct multiplet splitting. The observed splittings correspond to the spin–spin interaction of the unpaired p_z electron with the *ortho*- and *meta*-protons in the ring. Following the substitution of both *ortho*-positions of the carbenes by t-butyl groups or chlorine atoms, the signals become triplets.

At low temperature in an inert matrix, the signals of triplet carbene are observed virtually unchanged for a long time (1–1.5 h) in the absence of additional irradiation. This shows that the cyclohexadienone carbenes have a triplet ground state.

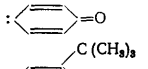
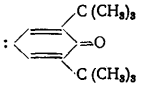
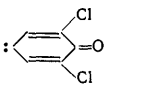
The reactivity of cyclic carbenes is determined by nucleophilic or electrophilic properties. Since the number of π electrons in the ring determines the net spin of the ground state of cyclic carbenes [14], appreciable differences are to be expected in their behaviour depending on the number of these electrons. In carbenes with the $(4n + 2)$

†The possibility of the generation of cyclohexadienone carbenes by the photolysis and thermolysis of arene diazo-oxides has been considered [11-13].

π-electron system the σ^2 configuration is stabilised and they have a singlet ground state with a vacant p_z orbital at the carbene centre. The vacant p_z orbital is incorporated in the overall π-electron system of the carbene molecule, which leads to the appearance of an enhanced electron density at the central carbon atom. Such carbenes are nucleophilic in the ground state. On the other hand, in carbenes with the $(4n)$ π-electron system the σ_p configuration is stabilised and they have a triplet ground state; such carbenes exhibit electrophilic properties.

In cyclohexadienone carbenes the incorporation of the p_z orbital of the central carbon atom in the overall π-electron system of the polyene part of the molecule leads to a shift of the p_z electron and the formation of an aromatic ring system. As a result, the electron density at the central carbon atom should fall. Their chemical behaviour resembles that of carbenes with the $(4n)$ π-electron ring system, i.e. they should be electrophilic. This conclusion is confirmed by ESR data [12,15-17]. The Table lists the splitting parameters of the energy levels of triplet methylenes at zero field. The D parameter characterises the spin–spin interaction of the unpaired electrons and is determined by the average value of the quantity $(1/r^3)$, [18,19] where r is the distance between the spins. This parameter may serve as a measure of the delocalisation of the p_z electron over the system of conjugated bonds and may characterise the electrophilic properties of the carbene centre. The Table shows that D is a minimum for cyclohexadienone carbene.

The splitting parameters of the energy levels of triplet methylenes at zero field.

Carbene	D, cm^{-1}	E, cm^{-1}	Valence angle, deg	References
$:CH_2$	0.6881	0.00346	136	15
$:CHC_6H_5$	0.5150	0.02510	140—155	16
$:C(C_6H_5)_2$	0.4055	0.01940	140—155	16
	0.4089	0.01200	—	17
	0.3179	0.00550	—	12
	0.3141	0.00510	—	12
	0.3284	0.00860	—	12

Since, according to its physical interpretation, the parameter D defines the probability of localising the unbound p_z electron at the bivalent carbon atom of the carbene, it follows (assuming identical distributions of π electrons in carbenes and the corresponding radicals) that the values of D for carbenes and the spin densities ρ_i for the radicals (at the same carbon atom) should be approximately the same [12,16]. Accordingly, as stated above, the π-electron system of cyclohexadienone carbenes is close to that of the corresponding phenoxy-radicals.

The parameter E characterises qualitatively the deviation of the spin–spin interaction from cylindrical symmetry and is therefore a criterion of the curvature of the methylene structure [20,21]. The E/D ratio corresponds to the contribution of the s orbital to the non-bonding sp^2 orbital of the bivalent carbon atom. For $E = 0$ $(E/D = 0)$, the contribution of the s orbital is zero, i.e. the non-bonding hybridised sp^2 orbital, located in the plane of the methylene molecule, is transformed into a pure p orbital and the methylene structure becomes linear (valence angle $\varphi = 180°$). Judging from the values of E quoted, in cyclohexadienone carbenes this angle should approach 180°. However, there is no reason to suppose that the valence angle differs appreciably from 120°. Presumably the σ bonds in the ring at the carbene centre are bent (a type of "banana bond"). In this structure for cyclohexadienone carbenes, ring strain is eliminated on the one hand and on the other there appears the possibility of a redistribution of the non-bonding σ electron among the neighbouring carbon atoms, which stabilises the carbene system as a whole.

III. THE MULTIPLICITY OF THE ELECTRONIC STATES OF REACTING CYCLOHEXADIENONE CARBENES

It was shown above that cyclohexadienone carbenes have a triplet ground state. However, the multiplicity of the ground state of the carbene frequently does not coincide with the multiplicity of its state when undergoing reaction. For synthetic use, it is essential to know the multiplicity of the electronic state of the carbene at the instant of its interaction with the substrate.

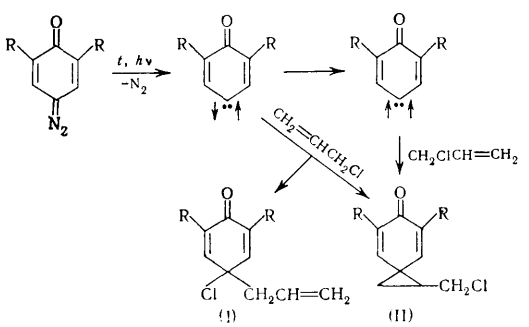
Chemical methods are nowadays widely used to determine the spin state of reacting carbenes. Thus the stereospecificity of the addition reactions of carbenes is due to the differences between the mechanisms of the interaction of the singlet and triplet forms of the carbene with the multiple bonds of *cis*- and *trans*-olefins (Skell's principle [22]). According to the majority of investigators, singlet carbenes add synchronously to the multiple bond without affecting the configuration of the initial olefin, while the triplet form reacts with formation of a trimethylene biradical, which leads to the formation of a mixture of the *cis*- and *trans*-adducts owing to the possibility of rotation about the C–C bond in the biradical (breakdown of stereospecificity). Studies on the interaction of cyclohexadienone carbenes with the multiple bonds in *cis*- and *trans*-olefins indicate a high stereospecificity of the addition (to an extent greater than 98%) in both thermal [24] and photolytic [23] formation of cyclohexadienone carbenes. This shows that the singlet form of the cyclohexadienone carbene is involved in the reaction.

Since cyclohexadienone carbenes have a triplet ground state, it follows, by analogy with gas-phase reactions, that, following the addition of an inert polyfluorinated solvent to the reacting substrate, the stereospecificity of the addition presumably breaks down in consequence of the $S \rightarrow T$ transition of the carbene when it collides with the molecules of the diluent. However, this effect (in a highly attenuated form only) was observed in the photolysis of arene diazo-oxides by filtered light at 0°C [23] and was completely absent in the thermolysis of arene diazo-oxides at 93–96°C. [24] The explanation is that at elevated temperatures the temperature conditions in the reaction, and not the effect of dilution by the polyfluorinated solvent, play a more significant role in the competition between two processes: the addition of singlet carbene to the multiple bond and the $S \rightarrow T$ transition.

The stereochemical method for the determining of the multiplicity of the electronic states of carbenes is in many cases ineffective, since, depending on the relative rates

of the intermediate stages, identical substances may be formed from both singlet and triplet carbenes [8]. For this reason, studies are now being made to discover rigorously specific reactions, which would proceed only with the triplet or singlet forms of carbenes. Research on competing reactions involving the addition of carbenes to multiple bonds and lone electron pairs of heteroatoms is extremely promising in this connection. Singlet carbenes can add both to a double bond and to lone electron pairs of a heteroatom. On the other hand, for triplet carbenes, as for other radical species, the mode of attack depends on the bond energies in the substance. Thus, in the reaction of triplet carbenes with olefins containing a halogen in the hydrocarbon chain, the double bond is most susceptible to radical attack. Consequently, the multiplicity of the electronic states of the reacting carbenes and the possibility of the $S \rightarrow T$ transition can be inferred from the change in the ratio of the yield of products resulting from the insertion of the carbene in carbon–halogen bonds to the yield of products formed as a result of the addition of the carbene to multiple bonds. This ratio decreases with increase of the fraction of the triplet form of the carbene and increases with increase of the fraction of the singlet form [25,26].

In order to investigate the multiplicity of the states of cyclohexadienone carbenes, a somewhat modified method of competition kinetics was employed [24]. The authors used allyl chloride as the substrate and, in order to increase the probability of the $S \rightarrow T$ transition, the temperature was reduced and allyl chloride was diluted with an inert solvent (hexafluorobenzene). The use of allyl chloride in the thermolysis and photolysis of 2,6-di-t-butylbenzene 1,4-diazo-oxide enabled the authors to obtain reaction mixtures consisting of a few final products suitable for spectroscopic analysis:

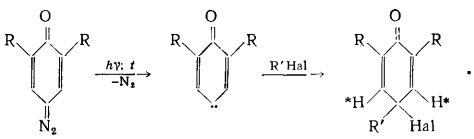


where R = $C(CH_3)_3$.

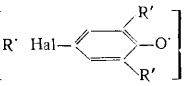
Analysis of ultraviolet spectroscopic and ^1H NMR data showed that the yields of the cyclohexadienone (I) and the spirodienone (II) and their ratio remain constant up to temperatures close to the glass point of allyl chloride. This shows that in the above temperature range the rate of reaction of the singlet carbene with allyl chloride greatly exceeds the rate of its singlet–triplet transition. With the formation of the allyl chloride matrix, the yield of I falls and that of II rises, which indicates an increasing role of the $S \rightarrow T$ transition. Evidently, on formation of the allyl chloride glass, the process becomes heterogeneous and takes place at the interface between the solid phases. The rate of reaction of the singlet carbene is now determined by its diffusion to the walls of the "cage" and may be close to the rate of the $S \rightarrow T$ transition. A further decrease of temperature tends to increase the difference between the rates of the chemical and physical processes. In contrast to the method involving a decrease of temperature, the use of the dilution technique leads to a very slight increase in the fraction of the triplet carbene. This agrees with data obtained in a study of the stereospecificity of the addition of cyclohexadienone carbenes to olefins.

In concluding this section, the possibility of employing the method of chemically induced dynamic nuclear polarisation (CIDNP) in the investigation of the multiplicity of the states of reacting carbenes must be considered. The polarisation of nuclei in the reactions of carbenes was observed for the first time by Closs and Closs [27]. Using the reactions of diphenylcarbene, they clearly formulated for the first time the idea of the selection of radicals in terms of their nuclear-spin states in the singlet–triplet transitions in radical pairs, which became the basis of the theory of the CIDNP method [28]. The method was used to investigate the thermolysis and photolysis of arene diazo-oxides [29-31].

The principal products of the thermolysis and photolysis of arene diazo-oxides in carbon tetrachloride and hexachloroacetone are the corresponding cyclohexadienone derivatives:



Their formation may be both a consequence of the rearrangement of the ylids arising in the interaction of the singlet carbene with the lone electron pairs of the halogen atom and of a radical process of the "abstraction-recombination" type. In the latter case both the singlet and triplet forms of the carbene may be responsible for the development of the reaction. Analysis of the ^1H NMR spectra of the reaction mixtures revealed a negative polarisation of the ring protons. This shows that the thermolysis and photolysis of arene diazo-oxides proceed via a radical mechanism with formation of the radical pair



as an intermediate, for which $g_{PhO\cdot} < g_{R\cdot}$ and $a_{meta} < 0$. According to the theory of CIDNP, the negative polarisation of the *meta*-protons in the recombination product of the radical pair arises when the pair was in a triplet state or when the pair was formed from the combination of independent radicals (a pair with non-correlated spins).

It was shown above that, under the usual conditions in the reaction with olefins, the carbenes are in the singlet state. Presumably cyclohexadienone carbenes also react in the singlet form with halogeno-derivatives. A singlet radical pair must then be formed initially. The radicals of this pair can recombine with the formation of cyclohexadienones or they can pass into the bulk phase, thereby producing pairs with non-correlated spins. In the former case positive polarisation of the *meta*-protons should be observed and in the latter negative polarisation. An overall polarisation has probably been observed [29-31], with the polarisation generated in the pairs with non-correlated spins predominating. This has been confirmed by experiments where radical acceptors (alkyl iodides) were added to the reaction medium [29,30]. The authors showed that, with increase of the concentration of alkyl iodides in the initial reaction mixture, the negative polarisation diminishes; at fairly high concentrations of alkyl iodides the sign of the polarisation is reversed. Evidently, following the

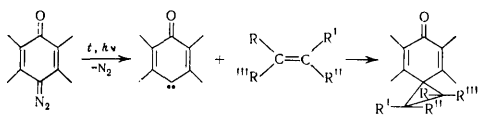
addition of alkyl iodides to the main solvent, the steady-state concentration of the radicals released into the bulk phase (particularly the $\cdot CCl_3$ and $\cdot CCl_2COCCl_3$ radicals) decreases and the contribution to the polarisation of the recombination of secondary radical pairs with non-correlated spins falls. The absorption by the *meta*-protons of cyclohexadienone compounds observed in the ^1H NMR spectra at high concentrations of alkyl iodides in the initial mixture arises because they are formed only from the primary singlet radical pairs. The polarisation of the ^{13}C nuclei[29,30] also confirms the primary formation of singlet radical pairs in the reactions of similar carbenes with hexachloroacetone.

Thus ESR and NMR data, the results of studies on the multiplicity of the states of cyclohexadienone carbenes by the method of competitive kinetics, and the high stereospecificity of their addition to the multiple bonds of olefins show that the carbenes have a triplet ground state and that under the usual conditions their reacting form is in the singlet state.

IV. REACTIONS OF CYCLOHEXADIENONE CARBENES

Addition to Multiple Bonds

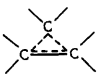
The interaction of cyclohexadienone carbenes with olefins has been most widely investigated[23,24,32-35]. The reaction with the multiple bonds of olefins of the cyclohexadienone carbenes produced by the thermolysis or photolysis of benzene 1,4-diazo-oxides results in the formation of the corresponding spirodienones containing the cyclopropane ring:



The maximum yields of the spiro-derivatives are obtained when olefins with a more nucleophilic double bond are used[32]. The introduction of functional groups into the olefin appreciably reduces the yield of the spirodienone, which is evidently associated with the ease of polymerisation of such olefins and with the difficulty of isolating the final products.

As mentioned above, cyclohexadienone carbenes add to stereoisomeric olefins with a high degree of stereospecificity[23,24,33]. Polarisation could not be observed in a CIDNP study of the thermolysis of 2,6-di-t-butylbenzene 1,4-diazo-oxide in hept-1-ene and cyclohexene [24], which confirms the conclusion that singlet carbene is involved in the reaction.

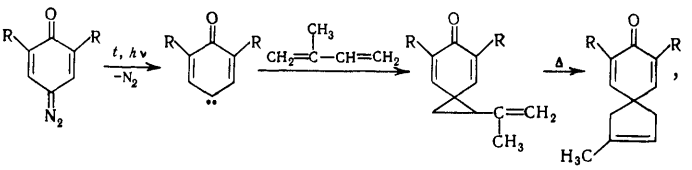
The single-stage addition characteristic of singlet carbenes is in reality more complex. The operation of dispersion forces, i.e. the interaction of the dipole moment of the carbene with the induced dipole of the olefin, leads to asymmetric addition. The non-synchronous formation of the two cyclopropane bonds is a characteristic feature of this process. Calculation shows[36] that, in the interaction of singlet methylene with ethylene, symmetrical addition is forbidden and the reaction pathway is asymmetric—it begins via an approximately π-electron mechanism and ends via an approximately σ-electron mechanism. The formation of a transition state with some sharing of the charge between the bivalent carbon of the carbene and the π bond of the olefin is then postulated:



The existence of a transition state having such a structure has been confirmed by kinetic data for dichloro- and difluoro-methylenes[37,38].

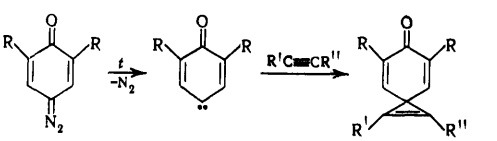
An alternative mechanism for the formation of spirodienones may involve the intermediate formation of unstable spiropyrazolones when the initial arene diazo-oxide adds to the double bond of olefins. Such adducts have been isolated in the thermolysis of 10-diazoanthrone in olefins[34]. However, this pathway is probably secondary and hardly occurs in the thermolysis and photolysis of benzene 1,4-diazo-oxides.

In the interaction of cyclohexadienone carbenes with the conjugated system of dienes, 1,2-addition to the most open double bonds might have been expected by analogy with other carbenes. However, cyclohexadiene carbenes behave in an unusual manner in this reaction—the final result is always the 1,4-addition product regardless of the presence and positions of substituents in the diene[39]. The formation of these products can be represented, on the one hand, as a result of direct 1,4-addition of the carbene to the conjugated bonds of the diene and, on the other hand, as a result of the isomerisation during the course of the reaction of the initially formed 1,2-addition product. A kinetic and spectroscopic study of the photolysis of 2,6-di-t-butylbenzene 1,4-diazo-oxide showed that in isoprene at low temperatures the second pathway is followed[39]. The authors succeeded in detecting spectroscopically and then in isolating the intermediate 1,2-addition product. Comparison of the kinetics of the isomerisation of this product and of the thermolysis of the 1,4-diazo-oxide in isoprene confirmed the proposed mechanism of the formation of the 1,4-addition product:



where $R = C(CH_3)_3$.

In contrast to double bonds, triple bonds do not exhibit a marked capacity for combination with electrophilic carbenes[40,41]. The yield of the corresponding cyclopropene derivatives in such reactions is as a rule low[40]. The reaction of cyclohexadienone carbenes with acetylenes leads to the formation of spiro[2,5]octa-1,3,6-triene-5-ones—cyclopropene derivatives of a new type in which the cyclopropene and cyclohexadienone rings are linked in a spiro-configuration[42-45]:

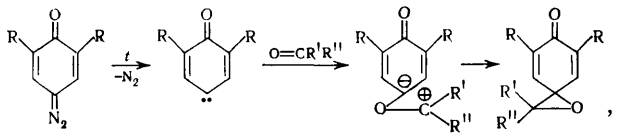


where $R = C(CH_3)_3$.

The yield of these derivatives does not exceed 40% and side products resulting from the insertion of the carbene in the C–H bond of the substituent are always present in the reaction medium.

The reactions involving the addition of carbenes to carbon–heteroatom multiple bond are less familiar because diazo-compounds can add directly to the C=X multiple bonds without the intermediate formation of carbenes. Furthermore, by no means every carbene is capable of attacking such a bond (for example, triplet carbenes). In a carbon–heteroatom multiple bond the heteroatom is usually more electronegative, i.e. behaves as the nucleophilic centre of the substrate. Consequently, depending on the electrophilic or nucleophilic nature of the bivalent carbon atom, singlet carbenes can initially attack either the heteroatom or the carbon atom in the C=X bond and identical compounds are formed in both cases.

When cyclohexadienone carbenes interact with aliphatic ketones, oxaspirodienones are formed as a result of the intramolecular stabilisation of the 1,3-dipolar ion[46,47]:



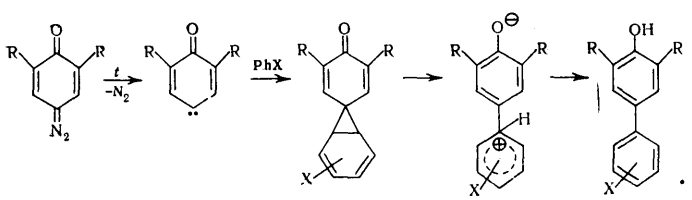
where R = $C(CH_3)_3$.

It is remarkable that oxaspirans are formed only when aliphatic ketones are used. The thermolysis of 2,6-di-t-butylbenzene 1,4-diazo-oxide in acetophenone and benzaldehyde gives rise to products resulting from insertion in the C–H bonds of the aromatic ring[47].

Interaction with Aromatic Compounds

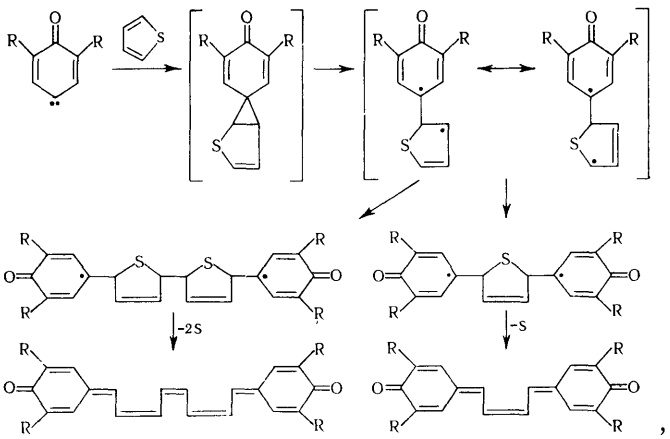
Such a reaction is characteristic of carbenes which are fairly electrophilic. It is generally accepted that it begins with attack by the carbene on the π-electron system of the aromatic compound. The further course of the reaction is determined by the stability of the intermediate norcaradiene structure. Depending on the nature of the attacking carbene, either a reversible norcaradiene–cycloheptatriene transformation is observed (the equilibrium is usually displaced towards the formation of the cycloheptatriene) or the norcaradiene structure is aromatised with formation of the formal product of insertion in the C–H bond of the aromatic ring. The latter process is more characteristic of cyclic carbenes with a π-electron system[48,49].

When cyclohexadienone carbenes interact with benzene derivatives, the main products are 4-arylphenols[50–59]. It is interesting that, when benzene derivatives are used, a mixture of isomeric 4-arylphenols is produced[55–57]. A number of investigators[51,55–58] observed the so called alcohol effect, which consists in an increased yield of 4-arylphenols when small amounts of alcohols are added to the aromatic substrate. The observed effects are explained satisfactorily by the reaction mechanism proposed by Dewar and Narayamaswami[57]:



The formation of the thermally unstable norcaradiene, which rearranges to the formal product of insertion in the C–H bond, constitutes an intermediate stage. The increase of the yield of 4-arylphenols following the addition of an alcohol is evidently associated with the increase of the lifetime of the singlet carbene owing to its stabilisation on formation of complexes with alcohol molecules. It is noteworthy that all attempts to detect the formation of the intermediate norcaradiene were unsuccessful[59]. However, the available experimental data show that the proposed reaction mechanism is the most likely.

This has been confirmed by studies on the interaction of cyclohexadienone carbenes with pyridine[51], thiophen[60,61], furan[62], and *N*-methylpyrrole[63]. In all cases the products are formed as a result of the addition of the singlet carbene to the multiple bonds of the substrate. The studies of the reactions with thiophens are the most interesting in this respect[60,61]:

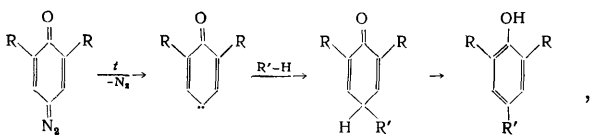


where R = $C(CH_3)_3$.

The reaction is accompanied by the formation of products not containing sulphur. Their composition can be satisfactorily accounted for by the above mechanism involving the formation of a spirodienone—the product of the addition of the carbene to a multiple bond of the thiophen.

Interaction with Hydrocarbons and Halogenohydrocarbons

The thermal decomposition of 2,6-di-t-butylbenzene 1,4-diazo-oxide in saturated cyclic hydrocarbons leads to 4-cycloalkylphenols. Their formation can be represented as a result of direct insertion of the cyclohexadiene carbene in the C–H bond of the hydrocarbon, resulting in the initial formation of an unstable quinolid compound, which readily isomerises to the phenol[54,64]:



where R = $C(CH_3)_3$. The absence of chemical polarisation in the phenol shows that the main process proceeds via a non-radical mechanism.

When alicyclic hydrocarbons are used in the reaction, a mixture of phenols is formed[64]. The low selectivity of the insertion reaction ($2^0 : 1^0 = 3.3$) is consistent with the hypothesis of the direct insertion of the singlet form of

the carbene in a C–H bond of the hydrocarbon. One should note that the reaction mixture contains stable compounds of the quinolid type, the formation of which can be accounted for by the partial transition of the carbene to the triplet state.

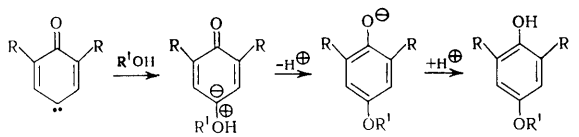
The reaction of cyclohexadienone carbenes with halogenohydrocarbons has provided wide possibilities for the synthesis of cyclohexadienone compounds, in which one of the geminal substituents is a halogen[29-31,65-67]. The interest in this reaction is due to the unusual mechanism of the insertion of carbenes in the carbon–halogen bond. In a series of studies, the reactions of cyclohexadienone carbenes with halogenohydrocarbons have been accounted for by an ylid mechanism[54,65]. The isolation of the intermediate ylid in the photolysis of 2,6-di-t-butylbenzene 1,4-diazo-oxide in 4-bromo-2,6-diazopropylphenol is quoted in support of this. The formation of side products is attributed to the $S \rightarrow T$ transition of the carbenes. However, as shown above, the $S \rightarrow T$ transition of cyclohexadienone carbenes is observed only in exceptional cases.

CIDNP data[29-31] showed that the process proceeds via a radical mechanism. The composition of the final products of the reaction of cyclohexadienone carbenes with halogenohydrocarbons is determined by their structure and the nature of the halogen. Thus, when carbon tetrachloride is used as the solvent, the main reaction product is a quinochloride. The replacement of one chlorine atom in CCl_4 by bromine or hydrogen leads to a complex composition of the reaction products[66]; nevertheless their formation is satisfactorily accounted by a radical mechanism.

Insertion in the O–H and C–O Bonds

Cyclohexadienone carbenes are electrophilic species and should therefore add to the lone electron pairs of heteroatoms with formation of intermediate ylid structures. From this standpoint, the mechanism of their insertion in the O–H and C–O bonds should be unique.

The study of the thermolysis and photolysis of benzene 1,4-diazo-oxide in aqueous[68], alcoholic[50,69], and acid media[69] showed that the main reaction products are the corresponding hydroquinones and the ethers and esters derived from them:



The main reaction is as a rule accompanied by radical side processes involving the dehydrogenation of the substrate and the formation of products derived from the phenoxy-radicals.

The composition of the products of the reaction of cyclohexadienone carbenes with the C–O bond of ethers depends on the structure of the initial arene diazo-oxide. Thus thermolysis of the unsubstituted arene diazo-oxide and of its dimethyl derivatives in tetrahydrofuran yields a mixture of high-molecular-weight products in which the arene diazo-oxide and ether fragments alternate[52,53]. On the other hand, in the thermolysis of 2,6-di-t-butylbenzene 1,4-diazo-oxide the main products are quinol spiro-ethers[70].

The characteristics of the electronic structure, the multiplicity of energy states, and the reactivity of cyclohexadienone carbenes discussed here show that carbenes of this type differ significantly from other bivalent carbon derivatives. Cyclohexadienone carbenes constitute an extremely convenient model for the investigation of the mechanisms of reactions involving the intermediate formation of methylene. The simplicity of the identification of the final products of their reaction with the substrate is of interest in connection with the development of methods for the determination of the multiplicity of the energy states of reacting carbenes. Finally, many of the reactions can be used successfully for the preparative synthesis of substituted phenols and their quinolid and spiran derivatives.

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