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Halogen-containing carbenes

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ABSTRACT. The electronic and steric influence of the substituents at a multiple bond and of the presence of a heteroatom in the molecule on the reactivity of compounds in relation to halogenocarbenes is examined. The mechanisms of the interaction of carbenes with single bonds are discussed and data on new methods for the generation of halogenocarbenes are reported.

The bibliography includes 140 references.

Contents

I. Introduction 654
II. Reactions with unsaturated compounds 654
III. Reactions with saturated compounds 658
IV. Reactions with compounds containing heteroatoms 659
V. Methods for the generation of halogenocarbenes 663

I. Introduction

Halogenocarbenes are used more often than other carbenes because of both their relatively ready availability and the synthetic importance of halogenocyclopropanes and other compounds obtained with the aid of halogenocarbenes. In terms of the extent to which these carbenes have been investigated as regards their thermodynamic properties, their structure (by quantum-chemical methods), and their simplest gas-phase reactions, this group of carbenes is inferior only to methylene and, partly, phenylcarbenes.

It has been shown in recent years that all mono- and di-halogenocarbenes have a singlet ground state. According to non-empirical calculations, the energy differences between the singlet and triplet states of carbenes are as follows (kJ mol^{-1}; the experimental values are given in brackets): CH_2 −46(−38);[1] CHF 55 ± 8 (< 63); CHCl 23 ± 8; CHBr 17 ± 8;[2] CF_2 205; CCl_2 71; CBr_2 46.[3] The enthalpies of formation ΔH_f^0 (singlet) of a number of carbenes have been determined experimentally (kJ mol^{-1}): CH_2 425 ± 2; CF_2 −180 ± 8; CClF 46 ± 4; CCl_2 238. We may also indicate the ionisation potentials of the same carbenes (eV): CH_2 (triplet) 10.396; CF_2 12.24 ± 0.01; CFCl 10.9 ± 0.3; CCl_2 9.76.[4] There have been numerous studies in which the geometrical structures of halogenocarbenes have been determined experimentally or calculated.[1–4]

This review deals with questions of the reactivity of halogenocarbenes generated in the liquid phase, namely the influence of electronic and steric factors and also the influence of the heteroatom in the substrate on the rate of reaction. Data are presented on new methods for the generation of halogenocarbenes.

II. Reactions with unsaturated compounds

This process has been investigated in greatest detail. The interaction of halogenocarbenes with unsaturated compounds leads to halogen-containing strained cyclic systems, which can be used as synthons in organic synthesis. On the other hand, this reaction is the simplest cheletropic process and has therefore attracted the attention of theoretical chemists.

1. The influence of the electronic effects

In order to determine the reactivity of double bonds in relation to halogenocarbenes, the method of competing reactions was already used in the first investigations. It was established that the relative rate constants are correlated with the σ^+ constants of the substituents in the aromatic ring for the reactions of dichlorocarbene with ring-substituted styrenes (−0.42),[5] 1-arylbuta-1,3-dienes (−0.42),[6] 2-arylbuta-1,3-dienes (−0.36),[7] 2-arylpropenes (−0.38),[8] 2-arylbut-1-enes (−0.37),[7] methyl esters of substituted cinnamic acids (−0.33), and arylideneanilines (−0.36).[9] The type of the correlation equation and the negative sign of the ρ constant (given above in brackets) indicate a transition state in which the reaction centre is positively charged and is involved in a direct polar conjugation with the substituent.

In the interaction with diene, triene, and tetraene hydrocarbons, dichlorocarbene adds to the terminal double bond. Its reactivity in the series buta-1,3-diene (0.48), *trans*-hexa-1,3,5-triene (1.27), styrene (1.0), 1-phenylbuta-1,3-diene (1.87), 1-phenylhexa-1,3,5-triene (2.02), 1-phenylocta-1,3,5,7-tetraene (2.02), and 2-phenylbuta-1,3-diene (4,38) is satisfactorily correlated with the localisation energies of the methylene carbon atom (L_r^+) calculated by the SCF PPP method as the difference between the energies of the π electrons of the hydrocarbon and the carbonium formed from it after the removal of the CH_2 fragment:[10,11]

$$\lg k_{\text{rel}}^{CCl_2} = -(0.57 \pm 0.05)L_r + 11.7; \quad r = 0.978; \quad s = 0.07, \; n = 7.$$

Similar correlations with the ionisation potentials (IP) have been observed for conjugated hydrocarbons ($\lg k = 4.53 - 0.53\text{IP}$; $r = 0.99$) and for non-conjugated hydrocarbons ($\lg k = 10.17 - 1.05\text{IP}$; $r = 0.99$).

For the estimation of the selectivity of the carbene, Moss proposed the carbene selectivity index m_{CXY} (relative to dichlorocarbene) calculated from the equation[12]

$$m_{CCl_2}^{CXY} = \lg (k_i/k_0)^{CXY} / \lg (k_i/k_0)^{CCl_2}. \quad (1)$$

The values of m_{CXY} can be calculated from the constants σ_R^* and σ_I of the substituents at the carbene centre by the equation[13,14]

$$m_{CXY} = -1.10 \sum_{XY} \sigma_R^+ + 0.53 \sum_{XY} \sigma_I - 0.31. \quad (2)$$

The selectivity of the carbene increases with increasing π-donor and σ-acceptor effects of the substituents at the carbene centre (Table 1). For $m_{CXY} \leqslant 1.5$, the carbene exhibits electrophilic properties (dihalogenocarbenes). Carbenes with nucleophilic properties [dimethoxycarbene, dimethylamino(methoxy)carbene] have a selectivity index $\geqslant 2.2$. Carbenes having a selectivity index in the range $1.5 < m_{CXY} < 2.2$ are ambiphilic: they react as electrophilic species with nucleophilic alkenes and they react as nucleophiles with an electrophilic double bond. Such carbenes include chloro(methoxy)carbene,[15,16] chloro(phenoxy)carbene,[17,18] fluoro(phenoxy)carbene,[19] and fluoro(methoxy)carbene.[13,14]

Table 1. The selectivity indices (m_{CXY}) of halogenocarbenes in reactions with alkyl- and aryl-ethylenes.

Carbene	Alkylethylenes				Arylethylenes	
	(1)	(2)	(3)	(4)	(1)	(2)
$BrCCO_2Et$	0.29	0.26	—	—	—	—
ClCClC=CCl_2	0.38*	0.34*	—	—	—	—
cyclo-C_3H_5CCl	0.41	0.73**	—	—	—	—
MeCCl	0.50	0.58	0.59	—	—	—
PhCBr	0.70	0.64	1.40 (0.50) ***	—	—	—
PhCCl	0.83	0.71	1.43 (0.59) ***	—	—	—
CBr_2	0.65	0.82	1.84	0.62	0.64	0.66
PhCF	0.89	0.96	1.59 (0.95)***	—	—	—
CFBr	0.96	1.18	—	1.03	0.80	0.83
CCl_2	1.00	0.97	0.98	1.00	1.00	1.00
CFCl	1.28	1.22	1.25	1.23	0.94	0.91
CF_2	1.48	1.47	1.48	1.43	0.83	0.79
ClCOMe	—	1.59****	—	—	—	—
ClCOPh	—	1.59****	—	—	—	—
FCOPh	—	1.74****	—	—	—	—
FCOMe	—	1.85	—	—	—	—

Note. The indices m_{CXY} have been calculated from Eqns. (1)–(4); the ratios k_i/k_0 in Eqn. (1) were taken from the literature.[13,14,22,23]

* According to the data of Kostikov and de Miegere.[20]

** According to Moss et al.,[21] the difference from the value obtained by Eqn. (1) is due to the different conformation of the carbene as a result of steric interactions.

*** Calculated for the conformation with the benzene ring rotated by 90°.

**** The ambiphilicity of carbenes was demonstrated.[15,19]

The dependence of the selectivity of the carbene on the series of alkenes selected for its determination has been demonstrated for the reactions of dihalogenocarbenes with alkylethylenes and styrenes.[5] Difluoro- and chlorofluoro-carbenes exhibit a greater selectivity in reactions with alkylethylenes than dichlorocarbene, while in reactions with ring-substituted styrenes they actually show a lower selectivity (Table 1).

Schoeller and co-workers[24–26] demonstrated within the framework of the one-electron perturbation theory that the selectivity index S can be defined by the following equation

$$S \equiv \partial(\Delta E)/\partial\Delta = \partial(\delta E_{\mathrm{I}} + \delta E_{\mathrm{II}})/\partial\Delta\,, \qquad (3)$$

where

$$\delta E_{\mathrm{I}} = \langle\pi|H|p\rangle^2 \cdot (E_p - E_\pi)^{-1};\ \delta E_{\mathrm{II}} = \langle\sigma|H|\pi^*\rangle^2 \cdot (E_\sigma - E_{\pi^*})^{-1};\ E_\sigma,\ E_p,\ E_\pi,$$

and E_σ, E_p, E_π, and E_{π^*} are the energies corresponding to the HOMO and LUMO of the carbene and the alkene. The selectivity indices calculated by Eqn. (3) are listed in Table 1. The values obtained agree well with the experimental data and data calculated by Eqn. (2). In the case of halogeno(phenyl)carbenes, a good agreement has been obtained for the conformation in which the benzene ring has been rotated by 90° (the values are given in brackets). The application of the molecular orbital perturbation method permits the calculation of the selectivity index of the carbene by means of the equation

$$m_{CXY} = d^X d^Y \Delta_{i0}^{CXY}/\Delta_{i0}^{CCl_2}, \qquad (4)$$

where d^X and d^Y are empirical constants of the substituents at the carbene centre, $\Delta_{i0}^{CXY} = (\varepsilon_{HOMO}^{i} - \varepsilon_{LUMO}^{CXY})^{-1} - (\varepsilon_{HOMO}^{0} - \varepsilon_{LUMO}^{CXY})^{-1}$ and ε_{HOMO}^{i}, ε_{HOMO}^{0}, and ε_{LUMO}^{CXY} are respectively the orbital energies of the HOMO of the ith and standard alkenes and of the LUMO of the carbene (Table 1).

Calculations by non-empirical methods have confirmed the dependence of the selectivity of the carbene on the relative positions of the frontier orbitals of the carbene and the alkene.[13] For electrophilic carbenes, the main contribution comes from the interaction of the unoccupied p orbital of the carbene with the HOMO (π) of the alkene, while for nucleophilic carbenes the main contribution is that of the interaction of the HOMO (σ) of the carbene with the LUMO (π*) of the alkene. For ambiphilic carbenes, the selectivity is appreciably influenced by the substituents at the double bond of the alkene: electron-donating substituents promote the manifestation of the electrophilic properties by the carbene, while electron-accepting substituents promote the manifestation of nucleophilic properties.

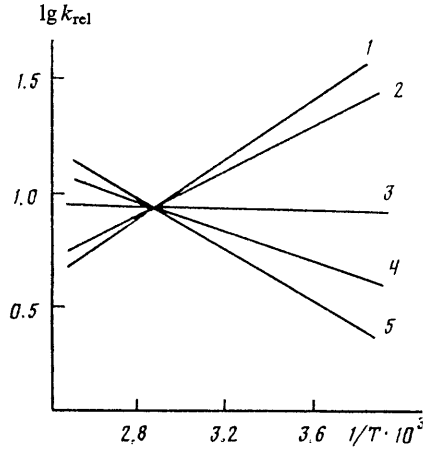


Figure 1. Temperature dependence of the relative reactivities of dihalogenocarbenes ($\lg k_{rel}$) for the 2,3-dimethylbut-2-ene/2-methylpropene pair[27]: *1*, :CF_2; *2*, :CFCl; *3*, :CCl_2; *4*, :CBrCl; *5*, :CBr_2.

The systematic study of the selectivity of dihalogenocarbenes at different temperatures undertaken by Giese and co-workers[27–29] demonstrated that the selectivity of dichlorocarbene in relation to the 2,3-dimethylbut-2-ene/2-methylpropene pair does not vary, while for

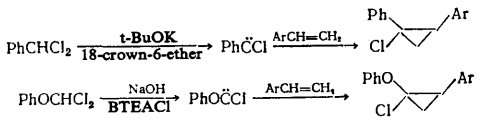
other carbenes it depends on temperature (Fig. 1). At 90° + 10 °C, the selectivity of all the dihalogenocarbenes is the same, while at higher temperatures fluorine-containing carbenes proved to be less selective than other carbenes but dibromocarbene is more selective. Thus, for the chosen pair of alkenes the reaction with dichlorocarbene can be assigned to the isoenthalpic series. This has to be set against the finding that the enthalpy of activation for the reaction of dibromocarbene with isobutene is higher than for the reaction with tetramethylethylene ($\Delta\Delta H^{*}$ = 6 kJ mol^{-1}). On the other hand, the enthalpy of activation for the reaction of difluorocarbene with isobutene is smaller than for the reaction with tetramethylethylene ($\Delta\Delta H^{\#}$ = −11 kJ mol^{-1}), which suggests that the entropy of activation plays the main role. The selectivity of dichlorocarbene in relation to the series of 2-arylpropenes is also independent of temperature ($\Delta\Delta H^{\#}$ = 0). On the other hand, the enthalpies of activation for the reactions of alkylpropenes increase with increase in the degree of branching of the alkyl group.[30] The selectivity index of dibromocarbene (m_{CBr_2}) depends on the degree of substitution at the double bond and assumes the following values: 1.1 for monosubstituted alkenes, 0.86 for disubstituted alkenes, and 0.73 for trisubstituted alkenes, which corresponds to the usual relation between activity and selectivity: a less reactive alkene exhibits a greater selectivity.[31]

Table 2. The relative rate constants for the reactions of chloro(phenyl)- and chloro(phenoxy)-carbenes with ring-substituted styrenes ($RC_6H_4CH=CH_2$) at different temperatures.[17,18]

R	PhCCl at different T (K)			PhOCCl at different T (K)			
	260	300	320	280	300	320	298*
p-MeO	1.44	1.65	2.22	0.42	0.74	0.83	1.95
p-Me	1.18	1.38	1.46	0.68	0.88	0.91	1.32
H	1.0	1.0	1.0	1.0	1.0	1.0	1.0
p-Cl	0.65	0.61	0.54	1.77	1.12	1.02	1.17
m-Br	—	—	—	2.39	1.53	1.24	—
ρ	−0.58	−0.76	−1.06	1.11	0.40	0.23	—

*Photolysis of chloro(phenoxy)diazirine.[17,18]

The selectivity of chloro(phenyl)carbene in reactions with styrene increases with increasing temperature,[32] while the selectivity of chloro(phenoxy)carbene, generated from dichloro(phenoxy)methane and NaOH, diminishes (Table 2):[33]



where BTEACl = benzyltriethylammonium chloride.

It may be that the different temperature dependences of the selectivities of these carbenes are because chloro(phenyl)carbene is electrophilic while chloro(phenoxy)carbene is nucleophilic. It has been shown[17,18] that chloro(phenoxy)carbene, generated by the photolysis of chloro(phenoxy)diazirine, is ambiphilic in the reactions with both styrenes (see Table 2; k_{rel} = 1.42 and 1.33 for *p*-trifluoromethylstyrene and *p*-nitrostyrene) and with other alkenes (for example, k_{rel} is 0.36 for hex-1-ene, 1.00 for pent-2-ene, 7.3 for isobutene, 3.0 for tetramethylethylene, 3.7 for methyl acrylate, and 7.3 for acrylonitrile).

The absolute rate constants for the interaction of arylhalogenocarbenes, generated by the flash photolysis of the corresponding arylhalogenodiazirines, with unsaturated compounds have been measured.[34] It follows from the temperature dependence of the absolute rate constants for the reactions of chlorophenylcarbene with a series of alkenes that the reactions have a negative ethalpy and entropy of activation and that the changes in the enthalpy of activation are responsible for the observed series of reaction rate constants (Table 3).[35]

Table 3. Thermodynamic parameters of the reactions of chloro(phenyl)carbene with alkylethylenes.[35]

Alkene	$\Delta\Delta H^{\#}$, kJ mol^{-1}	$\Delta\Delta S^{\#}$, J mol^{-1} K^{-1}	$\Delta\Delta G^{**}$, kJ mol^{-1}	k_{abs}^{*}, litre mol^{-1} s^{-1}	k_{rel}^{*}
2,3-Dimethylbut-2-ene	−18.4	−96	9.2	$3.3\cdot10^{8}$	1.0
2-Methylbut-2-ene	−15.5	−92	11.3	$1.6\cdot10^{8}$	0.48
trans-pent-2-ene	−6.6	−84	18.0	$1.0\cdot10^{7}$	0.030
Hex-1-ene	−6.3	−88	18.8	$3.8\cdot10^{6}$	0.012

* At 25 °C.
** From k_{abs}.

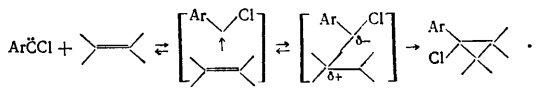
In order to account for the negative activation energy, the hypothesis was put forward that an intermediate complex between the carbene and the alkene is formed and that it can subsequently either decompose into the initial reactants or can give rise to cyclopropane. In all probability, this is either a π-complex of the carbene with the alkene or a "close pair" of the reactants in the solvent cage:

$$\ddot{\mathrm{C}}\mathrm{HCl} + \text{alkene} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \ddot{\mathrm{C}}\mathrm{HCl}/\text{alkene},$$

$$\ddot{\mathrm{C}}\mathrm{HCl}/\text{alkene} \xrightarrow{k_2} \text{cyclopropane},$$

$$k_{obs} = k_1 k_2/(k_{-1} + k_2).$$

The rate constants for the reactions of halogenophenylcarbenes with alkenes increase with increasing pressure in the reaction system and are independent of the solvent employed, which is consistent with the reversible formation of a carbene–alkene complex or an early transition state:



The introduction of electron-donating substituents into the aromatic ring stabilises the carbene and lowers its reactivity, while the introduction of electron-accepting substituents increases the reactivity (Table 4). Electron-accepting substituents favour the

conversion of the transition state into the final cyclopropane, stabilising the negative charge on the carbene atom, while the dissociation of the complex into the initial carbene and alkene is hindered. On the other hand, if the substituent is electron-donating, the degree of dissociation of the complex into the initial reactants increases. However, the data in Table 4 show that the selectivity of the carbene hardly changes when the substituent in the aromatic ring is altered. On the other hand, it does depend significantly on the character of the halogen atom at the carbene centre.[38] It is seen from Table 4 that the rate of addition to the double bond increases with decrease in the selectivity of the carbene in the sequence $F\ddot{C}Ph > Cl\ddot{C}Ph > Br\ddot{C}Ph$.

Table 4. The absolute rate constants for the addition of 4-$RC_6H_4\ddot{C}X$ to alkenes (k_{abs}, litre mol^{-1} s^{-1}) at 25 °C.[37,38]

X	R	10^6k			
		2,3-dimethyl-but-2-ene	2-methylbut-2-ene	*trans*-but-2-ene	hex-1-ene
F	H	160	53	2.4*	0.93
Br	H	380	180	12*	4.0
Cl	MeO	14	7.7	0.44	0.13
Cl	Me	120	49	1.8	0.62
Cl	H	280	130	5.5	2.2
Cl	Cl	330	180	7.5	2.3
Cl	CF_3	1500	680	49	18
$\rho(\sigma^+)$ for $RC_6H_4\ddot{C}Cl$		1.5	1.4	1.5	1.6

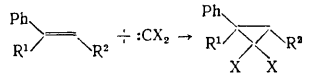
* Values for *trans*-pent-2-ene.

According to non-empirical calculations, complexes are not formed in the reactions of halogenocarbenes with alkenes (only complexes in a solvent cage are possible) and there is no activation barrier to cycloaddition.[39] The observed negative activation energies are probably a common feature of the reactions of all species with a high energy. In such cases the enthalpic activation barrier is absent and there is an entropic barrier. At low temperature, dichloro-, bromochloro- and dibromo-carbenes should then be non-selective and their reactions with alkenes should be diffusion-controlled.

The determination of the relative reactivities of deuterio-substituted 1-monosubstituted and 1,1-disubstituted ethylenes in relation to dichlorocarbenes showed that the "reverse" secondary isotope effect is observed for the CH_2 group in the given reaction ($k_H/k_D \simeq 0.73-0.80$), whereas for the CH group it is close to unity (0.90–0.94).[40] This result indicates a mechanism of the addition of the carbene to the C=C bond in which the carbene locks onto the methylene carbon atom of the double bond to a greater extent than onto the neighbouring atom.

2. The influence of steric effects

The study of reactions of dichloro- and dibromo-carbenes with α- and β-substituted styrenes showed that the reactivity of the double bond depends both on the type of its substitution and on the steric effects of alkyl groups:[41]



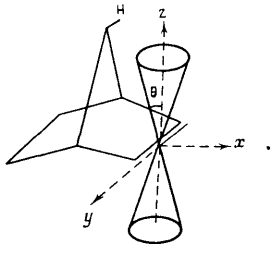
$$\lg k^{\beta}_{CCl_2} = -0.46 + 0.76 \lg k^{\alpha}_{CCl_2},$$
$$\lg k^{\alpha}_{CBr_2} = -0.20 + 0.84 \lg k^{\alpha}_{CCl_2},$$
$$\lg k^{\beta}_{CBr_2} = 0.94 \lg k^{\beta}_{CCl_2}.$$

The correlations obtained from the data in Table 5 between the reactivities of dichloro- and dibromo-carbenes show that α-alkylstyrenes are more sensitive than β-alkylstyrenes to changes in the substituent both at the double bond and at the carbene atom. This can be explained by the fact that in the transition state the carbene and the methylene group attacked by it are apparently in the *anti*-planar conformation.

Table 5. Relative rate constants k_{rel} for the reactions of substituted styrenes $Ph(R^1)C=CHR^2$ with dichloro- and dibromo-carbenes.[41]

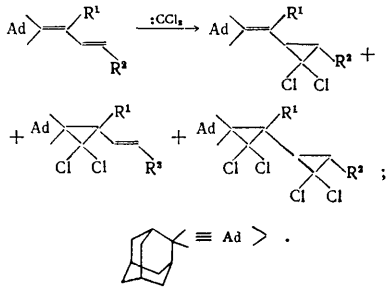
R^1	R^2	k_{rel}	
		CCl_2	CBr_2
Me	H	8.6±0.9	4.0±0.2
Et	H	5.7±0.4	2.6±0.2
iso-Pr	H	3.0±0.3	1.6±0.1
t-Bu	H	0.009±0.001	0.012±0.003
H	Me	1.9±0.2	1.8±0.2
H	Et	1.39±0.08	1.45±0.08
H	iso-Pr	0.67±0.03	0.69±0.05
H	t-Bu	0.010±0.005	—

The determination of the reactivities of the double bonds in bicyclic alkenes containing a *cis*-1,2-disubstituted C=C bond led to the conclusion that the approach of the carbene to the bond can be achieved only in a specific region of space, which can be represented by a cone whose axis (0*z*) passes through the centre of the double bond and is at right angles to it:[42]



The minimum angle of the cone (2θ) is about 60°. If any group (H atom) enters the cone located above the double bond, then the approach of the carbene is hindered. Fig. 2 presents the dependence of the reactivity of the double bond in relation to dichlorocarbene on the angle θ calculated for hydrogen atoms closest to the 0*z* axis for different molecules. With increase in the angle θ, the reactivity of the double bond rises, in agreement with the increase in the accessibility of the bond to the approach of the carbene. It is seen from the values of k_{rel} that the rate of addition of the carbene is a maximum for $\theta > 60°$ and that the reaction does not occur if $\theta < 30°$.

The additivity of the influence of the steric effects of the substituents at the double bond on the reactivity of the latter in the reaction of dichlorocarbene with adamantylidene-substituted 1,3-dienes and allenes has been established.[43] The reactivity of the double bond adjoining the adamantane ring is then low and mainly adducts involving the double bond remote from it are formed:



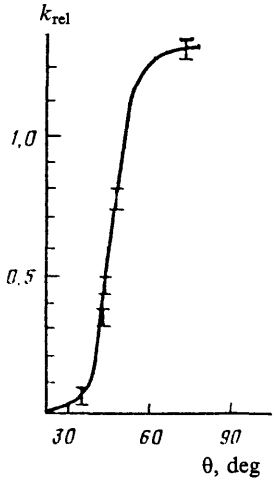
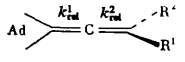


Figure 2. Dependence of the reactivity of the 1,2-disubstituted C=C bond on the angle θ.[40]

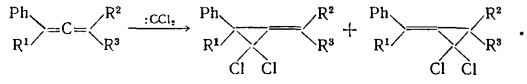
Comparison of the values of k_{rel} for allenes of the adamantane series shows that the reactivity of the double bond closest to the ring diminishes in proportion to the increase in the number of methyl groups at the C(3) atom, while the reactivity of the remote bond then increases.



R^1	R^2	k^1_{rel}	k^2_{rel}
H	H	0.47	0
H	Me	0.28	0.32
Me	Me	0	3.2

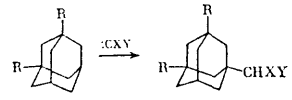
Comparison of the values of k_{rel} for the above allenes with model methylallenes has shown that the influence of the substituents at the C(3) atom of the allene system on the reactivity of the C(1)=C(2) bond can be represented by the equation $k_{rel} = (s'/s'')k_i$, where k_i is the relative rate constant for the reaction of the carbene with the C(1)=C(2) bond of the allene without a substituent at the C(3) atom and s' and s'' are coefficients taking into account the steric shielding of the double bond of the allene by the substituents at the C(3) atom from different sides of the plane of the C(1)=C(2) bond (s_H = 1, s_{Ad} = 0.36, s_{Me} = 0.16).

Adducts involving the most substituted double bond are formed exclusively in the interaction of dihalogenocarbenes with allene hydrocarbons containing aromatic substituents.[44] The reactivity of the bond adjoining the phenyl group can be estimated from the above equation in which the coefficient s for the substituents at the C(3) atom are 1.00 (H), 0.16 (Me), and 0.0 (Ph):

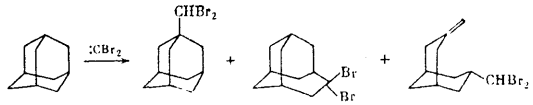


III. Reactions with saturated compounds

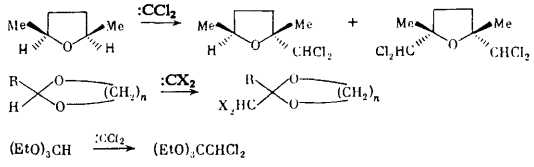
The interaction of halogenocarbenes with single bonds has been investigated much less than the interaction with a double bond. Halogenocarbenes are inserted fairly readily only in a tertiary C–H bond. Thus the reaction of dichlorocarbene, generated under phase-transfer conditions, with adamantane and 1-methyl- and 1,3-dimethyladamantanes leads to the formation of insertion products in high yields.[45] The reaction of dibromocarbene with adamantane results in the formation, apart from the product of insertion in a tertiary C–H bond, also of products involving the expansion and cleavage of the ring:[47]



R=H, Me, X=Y=Cl (Ref.45);
R=H, X=Y=Br (Ref.45);
R=H, X=Cl, Y=CCl=CCl$_2$ (Ref.46).



Dihalogenocarbenes are inserted, with moderate yields, in the C–H bonds of alkyl-substituted aromatic hydrocarbons: ethylbenzene, cumene, and diphenylmethane.[48,49] The carbene is easily inserted in a C–H bond in the α-position with respect to a C–O bond, for example in tetrahydrofuran,[50] dioxolan,[51,52] dioxane,[52] and ethers:[51]

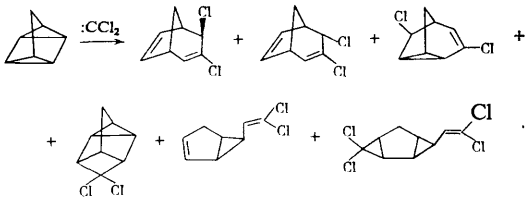


The interaction of dichlorocarbene with alkoxides leads to products of the insertion of the carbene in the α-CH bond in satisfactory yields:[53]

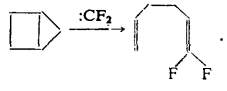
$$RCH_2OLi \xrightarrow[THF]{CHCl_3,\ t\text{-}BuOLi} RCH(OH)CHCl_2,$$

R=Ph, CH=CH$_2$, CH=CHPh.

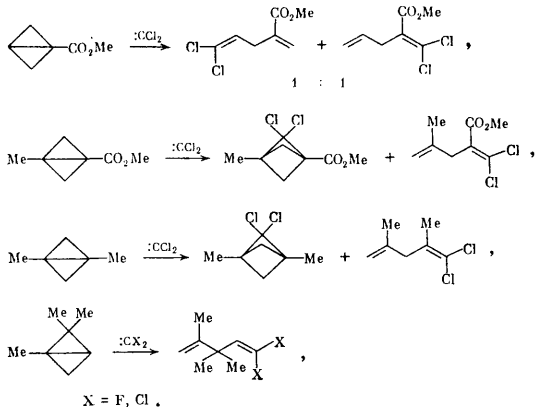
The interaction of dihalogenocarbenes with quadricyclane affords a low yield of a mixture of the same adducts as with norbornadiene but in other proportions:[54,55]



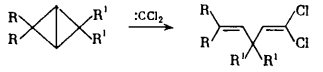
Difluorocarbene, generated from bromodifluoromethyltriphenylphosphonium bromide in the presence of KF, reacts with bicyclo[2.1.0]pentane, producing a very low yield (0.5%) of 1,1-difluorohexa-1,5-diene.[56] An adduct is not formed with bicyclo[3.1.0]hexane:



The interaction of 1,3-disubstituted bicyclobutane derivatives with dichlorocarbene leads to bicyclo[1.1.1]pentane or penta-1,4-diene derivatives depending on the nature of the substituents. The methyl ester of bicyclobutane-1-carboxylic acid reacts with dichlorocarbenes, forming only 1,1-dichloro-2-methoxycarbonylpenta-1,4-diene and the corresponding 4-methoxycarbonyl derivatives,[57] the reaction of the methyl ester of 3-phenylbicyclobutane-1-carboxylic acid gives rise to bicyclopentane derivatives, while the methyl ester of 3-methylbicyclobutane-1-carboxylic acid affords a mixture of substituted bicyclopentane and penta-1,4-diene.[58,59] The reaction of 1,3-dimethylbicyclobutane with dichlorocarbene produces a mixture of 2,2-dichloro-1,3-dimethylbicyclo[1.1.1]pentane and 1,1-dichloro-2,4-dimethylpenta-1,4-diene, whose ratio depends on the method of generation of the carbene.[60] The reaction of 1,2,2-trimethylbicyclobutane with both dichlorocarbene[61] and difluorocarbene[56] produces only a 1,1-dihalogeno-3,3,4-trimethylpenta-1,4-diene:



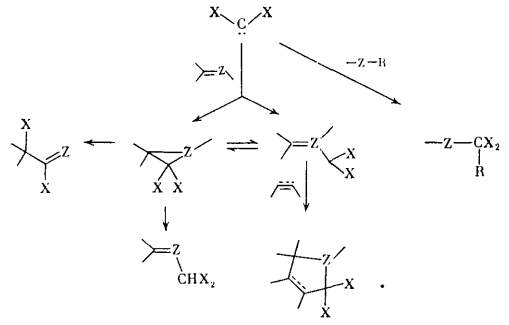
The reaction of 2,2,4,4-tetraalkylbicyclobutanes with dichlorocarbene afford only substituted penta-1,4-dienes:[62]



According to quantum-chemical calculations, the interaction of singlet carbene with bicyclobutane can proceed as a result of the attack by the free 2*p* orbital of the carbene on the HOMO of the bicyclobutane, which is located mainly on the C(1)–C(3) bond. The approach of the carbene "from the side", leading to the formation of penta-1,4-diene, is then more favourable than attack "from above", which leads to bicyclopentane.[56]

IV. Reactions with compounds containing heteroatoms

When the molecule contains a heteroatom having an unshared electron pair, the carbene can interact with the latter, forming an ylide. The possible pathways in the reactions of a carbene with compounds containing a heteroatom are indicated schematically below:



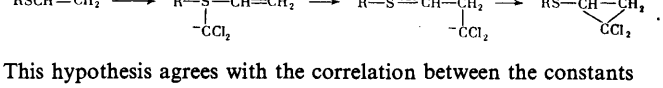
1. Oxygen- and sulphur-containing compounds

The ethers of 2,2-dihalogenocyclopropanols are formed in the reactions of dihalogenocarbenes with vinyl ethers.[63,64] In their reactions with dichlorocarbene, vinyl ethers are 10–20 times more reactive than the corresponding carbon analogues (alk-1-enes), which indicates an appreciable mesomeric involvement of the oxygen atom in the stabilisation of the transition state. It has been shown for a series of α-heterosubstituted styrenes $PhCX=CR^1R^2$, where X = OAlk, Cl, or Br, that the following relation holds:[65]

$$\lg k_{rel} = 10.41 - 18.2\ 2\Delta\varepsilon_j - 2.16m,$$

where $\Delta\varepsilon_f = \varepsilon_{\text{styrene HOMO}} - \varepsilon_{\text{carbene LUMO}}$ and m is the number of substituents at the β-carbon atom of the double bond.

The interaction of dichlorocarbene with unsaturated sulphides affords both cyclopropane derivatives[66,67] and the products of the dehydrochlorination of the latter.[67,68] Table 6 lists the relative rate constants for the addition of dichlorocarbene to vinyl ethers and vinyl sulphides. It is seen from these data that vinyl sulphides are 5–6 times more reactive than the corresponding vinyl ethers. This result cannot be explained solely by the different electronic influences of the group RX on the double bond. In its reactions with the sulphides, dichlorocarbene probably interacts not with the double bond but with the sulphur atom, forming an ylide, which then undergoes a 1,3-sigmatropic shift, affording a dipolar ion, which cyclises to cyclopropane:[69]

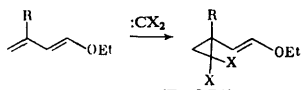


This hypothesis agrees with the correlation between the constants k_{rel} for the reactions of dichlorocarbene with vinyl sulphides, on the one hand, and the ionisation potentials of the unshared electron pair (IP) and the coefficient c_S of the sulphur atom involved in the

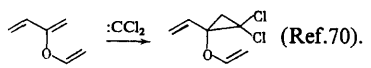
HOMO of the sulphides, on the other, in accordance with the equation

$$\lg k_{rel} = -(4.79 \pm 0.5) + (17.8 \pm 1.7) c_S^2/(IP - 6.8).$$

In reactions of dihalogenocarbenes with dienes containing an alkoxy-group, the carbene adds to the double bond at the end of the conjugation system or to a "cross-conjugated" bond:



R = H, Me; X = Cl (Ref.71)
R = H, X = Br (Ref.72)



In the reactions with dichloro- and dibromo-carbenes, 1,1-diethoxy-ethylene produces cyclopropanone ketals, which are converted into halogenoacrylic acid esters on heating. On the other hand, the spirocyclic dibromoketal is stable and can be used in syntheses:[73]

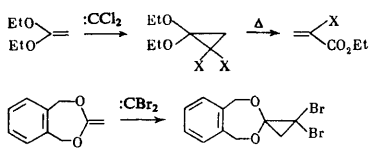
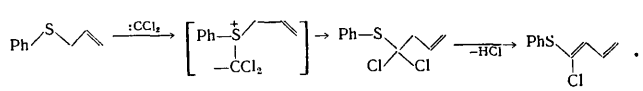


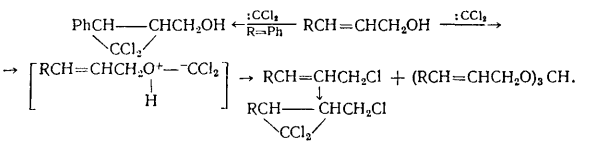
Table 6. The relative rate constants for the addition of dichlorocarbene to sulphides and ethers of the type $RXCH=CH_2$ relative to cyclohexene.

R	k_{rel}	
	X=S (Ref.69)	X=O (Ref.70)
Me	7.1	1.5
Et	—	1.7
n-Bu	10.1	1.7
iso-Bu	8.2	1.4
t-Bu	5.5	6.2
Ph	3.3	0.69
$CH_2=CH$	2.9	0.6

The interaction of dichlorocarbene, generated by the phase-transfer method, with allyl phenyl sulphide led to the isolation of 1-chloro-1-phenylthiobuta-1,3-diene,[74] obtained as a result of the dehydrochlorination of the product of the [2,3]sigmatropic rearrangement of the ylide:

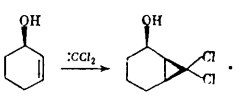


Dichlorocarbene, generated by the phase-transfer method, reacts with substituted allyl alcohols to form substituted (2,2-dihalogeno-cyclopropyl)carbinols in high yields.[75] The thermolysis of (bromodichloromethyl)phenylmercury in allyl alcohol yields allyl chloride, allyl formate, and chloroform.[76] The interaction of dichlorocarbene, generated under the conditions of phase-transfer catalysis, with allyl and cinnamyl alcohols proceeds via two pathways, involving the double bond and the hydroxy-group; in the case of allyl alcohol, 2,2-dichloro-1-chloromethylcyclopropane, triallyloxymethane, and allyl chloride are formed. The main product of the reaction with cinnamyl alcohol is 3,3-dichloro-1-hydroxy-methyl-2-phenylcyclopropane; in addition, 3-chloro-1-phenylprop-1-ene and 3,3-dichloro-1-chloromethyl-2-phenylcyclopropane are formed:[77]

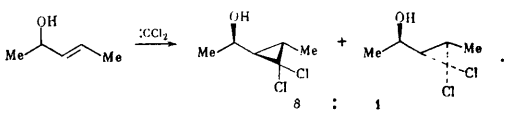


It has been shown by the methods of competing reactions that the ratios of the activities of the hydroxy-group (in both alcohols) and double bonds in cinnamyl alcohol, allyl alcohol, cinnamyl chloride, and allyl chloride are approximately 1 : 1.2 : 0.04 : 0.3 : 0.01 in reactions with dichlorocarbenes.

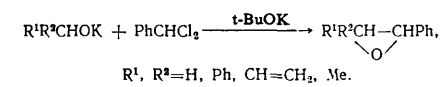
The reactions of cyclic allyl alcohols with dichlorocarbene readily give rise to dichlorocyclopropane derivatives. In conformity with the directing effect of the hydroxy-group, the reaction of 2-cyclohexenol gives rise to a mixture of the *syn*- and *anti*-products in proportions of 13 : 1, whereas 2-cycloheptanol and 2-cyclooctenol afford only the *anti*-adducts:



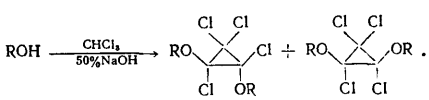
In the case of acyclic allyl alcohols, the most stable rotational isomer is converted into a dichlorocyclopropane and the reaction takes place predominantly from the side of the hydroxy-group:[78]



Chloro(phenyl)carbene, generated from benzylidene dichloride on treatment with potassium t-butoxide, reacts with alkoxides to form oxirans:[79]

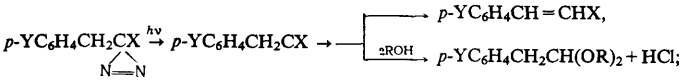


When dichlorocarbene was generated by the phase transfer method using ethanol-containing chloroform, 1,1,2,3-tetrachloro-2,3-diethoxycyclopropane was obtained.[80] A mixture of stereoisomeric 2,3-dialkoxy-1,1,2,3-tetrachlorocyclopropanes is also formed in the reactions with isobutyl and neopentyl alcohols,[81] while benzyl and phenylethyl alcohols afford the corresponding ortho-esters:



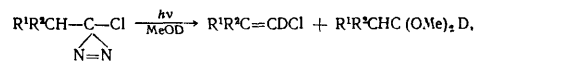
It follows from kinetic experiments that the reaction of benzylchlorocarbenes, obtained from the corresponding diazirines, with alcohols involves the insertion of the carbene in the O—H bond

of the alcohol dimer or oligomer via the electrophilic attack of the carbene on the unshared electron pair of the oxygen atom with the reversible formation of an ylide intermediate:[82,83]



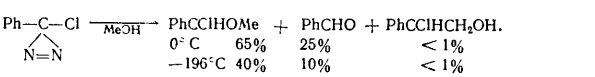
X=Cl, Br; Y=H, Me, Cl;
R=Me, Et, CH_2.

The study of the reactions of substituted benzylchlorocarbenes with MeOD showed that the carbene is partly protonated by the alcohol and that the subsequent elimination of the proton leads to an alkene or an ether:[84]

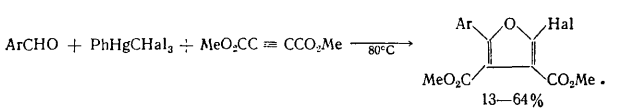


R^1=Ph, $PhCH_2$, PhO, R^2=H, Me.

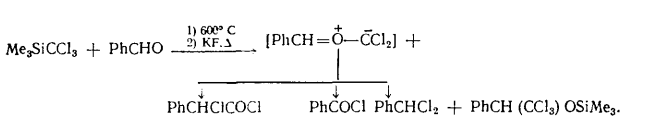
The photolysis of chloro(phenyl)diazirine in methanol at 0 °C and in a matrix at –196 °C showed that an increase in the yield of the products of the insertion of singlet chloro(phenyl)carbene in a C–H bond is not observed when the temperature is reduced and the principal reaction pathway remains the insertion in the O–H bond:[85]



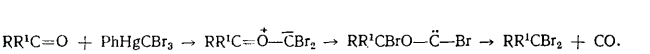
In the reactions of dichloro- and dibromo-carbenes, generated from phenyltrihalogenomethylmercury derivatives, with benzaldehydes, dihalogenocarbonyl ylides are formed. These have been detected in reactions with dipolarophiles:[86,87]



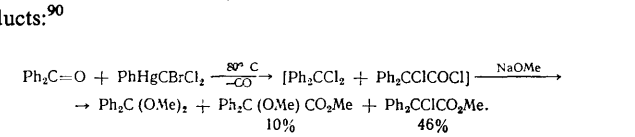
Vacuum flash pyrolysis of Me_3SiCCl_3 involves the formation, together with benzaldehyde, of dichlorocarbonyl ylide,[88] which then reacts according to the following mechanism:



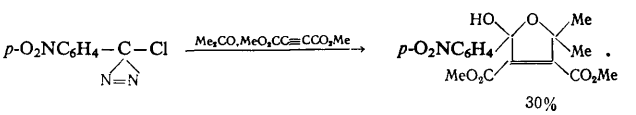
When $PhHgCBr_3$ is heated in the presence of aldehydes and ketones, a deoxygenation reaction is observed:[89]



In contrast to the reactions of dichlorocarbene derived from $PhHgCBrCl_2$ with aromatic aldehydes, it was not possible to detect carbonyl ylides in the reactions with aromatic ketones.[90] It has been suggested that for steric reasons the latter are readily converted in this instance into oxirans, whose reactions lead to the final products:[90]

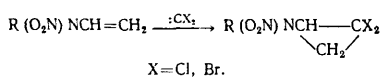


The reaction of chloro(*p*-nitrophenyl)carbene with acetone produces an ylide, whose formation has been detected by means of the reactions with dipolarophiles:[91]



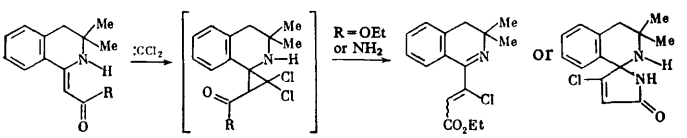
2. Nitrogen-containing compounds

Substituted aminocyclopropanes have been obtained in the reactions of halogenocarbenes with enamines. The reactions of *N*-nitroenamines with dichlorocarbenes[92] and dibromocarbenes[92,93] lead to the formation of the corresponding dihalogenocyclopropanes in yields ranging from 20 to 60%:

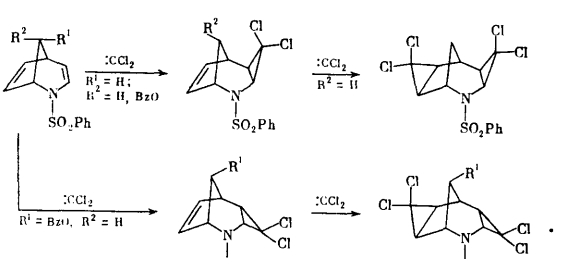


X=Cl, Br.

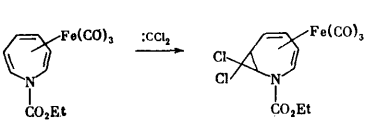
The dichloropropanes formed in the interaction of dichlorocarbene with 1-(R-carbonylmethylene)-3,3-dimethyl-1,2,3,4-tetrahydroisoquinolines are converted into a 1-azadiene or a spirolactam under the reaction conditions:[94]



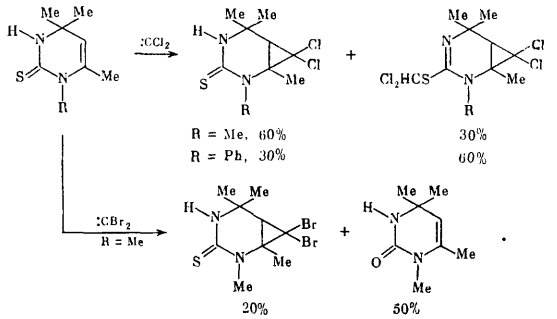
The influence of the stereochemistry of the enamine on the stereoselectivity of the cycloaddition of dihalogenocarbenes has been investigated. *N*-(Benzenesulphonyl)-2-azabicyclo[3.2.1]octa-3,6-dienes react with dichlorocarbene predominantly via the C(3)=C(4) bond, whereupon the stereochemistry of the cycloaddition is determined by the substituent at the C(8) atom:[95]



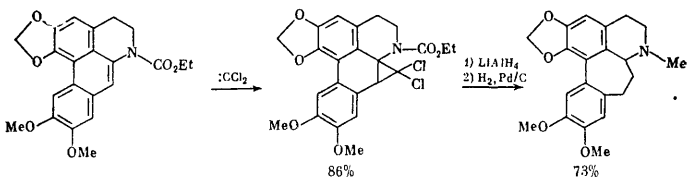
The addition of dichlorocarbene to tricarbonyl[*N*-(ethoxycarbonyl)-azepine]iron takes place selectively:[96]



The reactions of 1-substituted 4,4,6-trimethyl-1,4-dihydropyrimidine-2(3*H*)-thiones with dihalogenocarbenes lead to the corresponding cyclopropane derivatives:[97]



The addition of dichlorocarbene to the enamine double bond with subsequent ring expansion has been used to synthesise homoaporphines:[98]

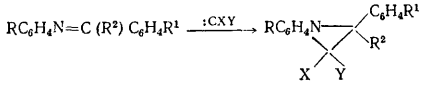


A similar strategy, involving the addition of a dihalogenocarbene to the double bond in 1,2-dihydroisoquinolines and subsequent cleavage of the three-membered ring at the bond opposite to the CX_2 group, has been used in the synthesis of benzazepines.[99–101] In these cases, the dihalogenocarbene added to the enamide group:

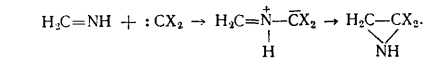


R', R² = O, R³ = Me; R' = H, R² = Ph, R³ = Ac; X = Cl, Br.

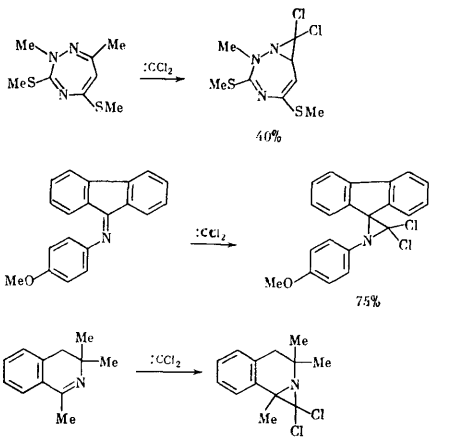
The reactions of bromine-, fluorine-, and chlorine-containing dihalogenocarbenes with aromatic azomethines, leading to the formation of *gem*-dihalogenoaziridines, have been studied in detail.[9] The relative reactivities of the azomethines in the reactions with dibromo- and dichloro-carbenes are then correlated with the basicities of the azomethines. Asymmetric carbenes react stereoselectively:[9]



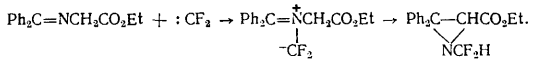
Quantum-chemical calculations for the interaction of methylene and dichlorocarbene with formaldimine have shown that in all cases the reaction begins with the formation of an ylide (without an activation barrier), which then cyclises to aziridine with a small activation barrier:[102]



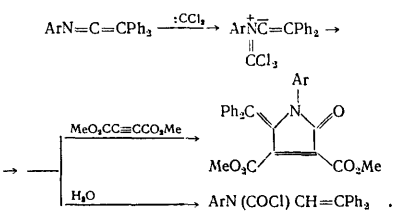
Dichlorocarbene reacts with *trans*-cinnamylideneaniline only at the C=N bond with formation of 3,3-dichloro-1-phenyl-2-(*trans*-2-phenylvinyl)aziridine.[9] 2,2-Dibromo-3-(4-nitrophenyl)-1-phenylaziridine[103] as well as a substituted triazepine[104] and spirocyclic aziridines[94,105] have been synthesised by the reactions of azomethines with dihalogenocarbenes generated under the conditions of phase-transfer catalysis:



The reactions of acetophenone anils with dichlorocarbene, generated by treating $CHCl_3$ with potassium t-butoxide, afforded the corresponding *gem*-dichloroaziridines in 40–80% yields.[106] Perfluorinated carbenes do not form aziridines on reaction with fluorinated azomethines, while $(CF_3)_2C{=}NH$ reacts with bis(trifluoromethyl)carbene to give the product of insertion in a H–N bond.[107] On the other hand, the reaction of difluorocarbene with the imine derivative of glycine leads to an aziridine, which is formed as a result of the rearrangement of the primary difluoroazomethine-ylide:[108]

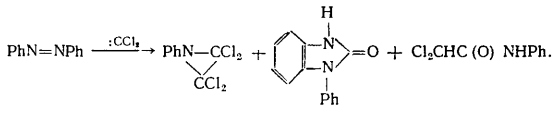


The reactions of keten imines with dichlorocarbene, generated by the thermal catalytic decomposition of sodium trichloroacetate, involve only the C–N bond and lead to the formation of the corresponding carbamoyl chlorides as a result of the hydrolysis of the intermediate keten imine-ylides.[109,110] The relative reactivities of compounds containing cumulated C=C and C=N bonds in the reactions with dichlorocarbene, obtained from chloroform and potassium t-butoxide at 0 °C (k_{rel} is 1.0 for $PhN{=}C{=}CPh_2$, 0.7 for p-$ClC_6H_4N{=}C{=}CPh_2$, 1.1 for p-$MeOC_6H_4N{=}C{=}CPh_2$, and 0.44 for PhN=CHPh), have been measured for the first time.[110] The formation of keten imine-ylides has been confirmed by their reactions with olefinic and acetylenic dipolarophiles:[111]

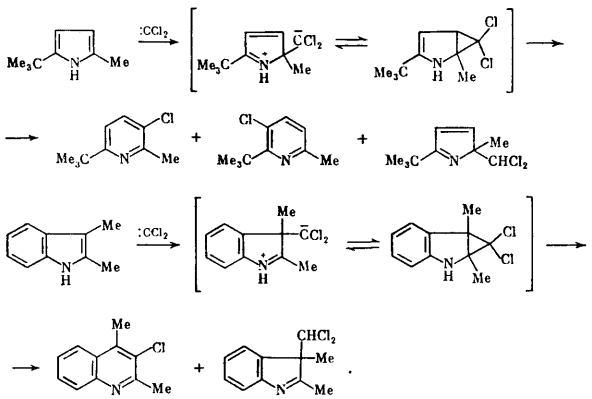


1-Phenylbenzimidazol-2-one has been isolated in the reaction of azobenzene with dichlorocarbene, generated under the conditions of phase-transfer catalysis together with tetrachloroaziridine, which is also formed in the reactions of azobenzene with phenyltrihalogenomethylmercury reagents.[112,113] 1-Phenylbenzimidazol-2-one is

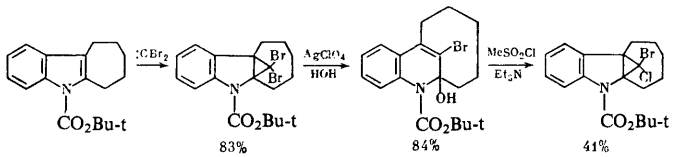
formed via the intermediate *gem*-dichlorodiaziridine:



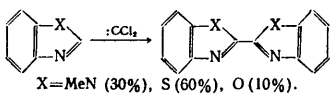
The study of the mechanism of the interaction of dichlorocarbene, generated from $PhHgCCl_3$ and NaI, with 2,5-dialkylpyrroles and 2,3-dialkylindoles[114,115] showed that, in a neutral (aprotic) or weakly alkaline (protic) medium, the reaction proceeds via the same intermediate:



In the reaction of dibromocarbene with cycloheptenoindole, a tetracyclic adduct was obtained and was converted by a ring opening process into the corresponding dihydroquinoline, undergoing an unusual retrocyclisation:[116]

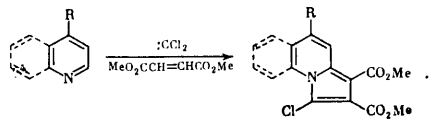


In dichlorocarbene generating systems, benzazoles afford bibenzazoles:[117]

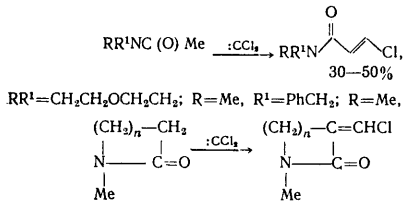


X=MeN (30%), S (60%), O (10%).

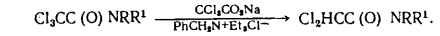
It has been established recently that six-membered azaheterocycles react with dichlorocarbene to form unstable cyclic immonium ylides, whose cycloaddition leads to 3-chloroindolizines which are otherwise difficult to obtain:[118]



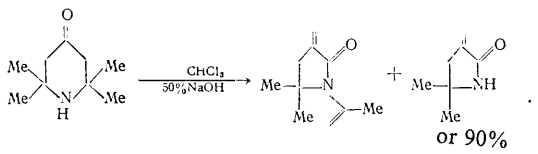
The corresponding (*E*)-3-chloroacetamides and α-chloromethylenelactams have been obtained from tertiary acetamides and lactams:[119]



Under the conditions of the thermal catalytic decomposition of sodium trichloroacetate in chloroform, trichloroacetamides are reduced to dichloroacetamides as a result of the chlorophilic CCl_3 elimination reaction:[120]

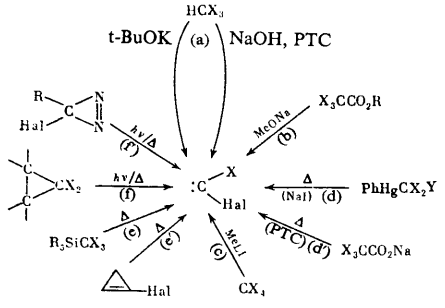


The interaction of dichlorocarbene with 2,2,6,6-tetramethylpiperidin-4-one results in ring contraction:[121,122]



V. Methods for the generation of halogenocarbenes

Numerous methods for the preparation of halogenocarbenes are now known. A general scheme illustrating the methods of generation is presented below and includes the following: (a) classical methods for the formation of dihalogenocarbenes from haloforms with the aid of potassium t-butoxide or 50% sodium hydroxide solution in the presence of a phase-transfer catalyst (PTC): (b) treatment of trihalogenoacetic acid esters with sodium methoxide: (c) the interaction of organolithium compounds with tetrahalogenomethanes: (d) thermal decomposition of phenyltrihalogenomethylmercury derivatives or sodium trihalogenoacetates (a catalyst may be used to reduce the temperature at which the decomposition takes place): (e) thermal decomposition of trihalogenomethylsilyl derivatives or 1-halogenocyclopropenes: (f) the photolysis or thermolysis of halogenocyclopropanes or halogenodiazirines.



Halogenocarbenes can be generated in this way in both neutral and alkaline media and thermolysis or photolysis can be used for this purpose.

New ways of generating halogenocarbenes appeared recently and these will be examined below.

Dichlorocarbene has been obtained by treating CCl_4 with KOH in t-butyl alcohol and dimethyl sulphoxide.[123] The addition of carbene to alkenes takes place stereospecifically and the yields of cyclopropanes are 48–93%.

Dichlorocarbene is formed under the conditions of phase-transfer catalysis from trimethylsilyl trichloroacetate in the presence of KF.[124] The yields of cyclopropanes reach 70% when CH_2Cl_2 is used as the solvent and $NBu_4^+I^-$ or 18-crown-6-ether are used as catalysts. Dichlorocarbene is also formed in the vacuum flash thermolysis of trimethyl(trichloromethyl)silane at 600 °C.[88] Dichloro- and dibromo-carbenes have been generated by the photolysis of 11,11-dichloro- or 11,11-dibromo-tricyclo[4.4.1.0^{1,6}]-undeca-2,4,8-triene at 25 °C; the yield of the corresponding cyclopropanes in the reaction with cyclooctene reaches 80%.[125]

New methods have been proposed recently for the generation of difluorocarbenes—for example, by the reaction of phosphines and phosphites with bromodifluoromethyl(triphenyl)phosphonium salts:[126]

$$Ph_3P^+CF_2BrBr^- + Ph_3P + Me_2C{=}CMe_2 \rightarrow \underset{\underset{CF_2}{\diagup\diagdown}}{Me_2C{-}CMe_2}\ ,\quad 35\%$$

Difluorocarbene, obtained from the complex $(CF_3)_2Cd.glyme$, reacts stereospecifically with alkenes:[127]

$$(CF_3)_2Cd.glyme + AcBr + Me_2C{=}CMe_2 \xrightarrow{-30^\circ C} \underset{\underset{CF_2}{\diagup\diagdown}}{Me_2C{-}CMe_2}\ (70\%) + AcF\ (96\%)\ .$$

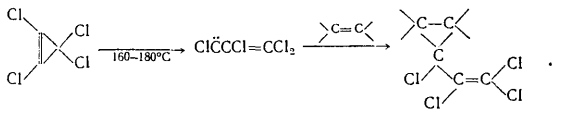
The mechanism of the generation of $:CF_2$ from $PhHgCF_3$ on treatment with the iodide anion has been investigated.[128] The formation of difluorocarbene has been postulated in the reaction of HCF_2SO_2F with nucleophiles.[129] The interaction of HCF_2SO_3H with P_2O_5 yielded $HCF_2SO_3CHF_3$, which was formed as a result of the insertion of $:CF_2$ in the initial compound.[130] The influence of the conditions in the reaction of HCF_2SO_2R (R = F, OPh, $OCH_2CF_2CHF_2$, C_6F_5, $OCHF_2$, NHPh, or NMePh) with bases and acids on the intermediate formation of difluorocarbene, the latter giving rise to an adduct with 2,3-dimethylbut-2-ene, has been investigated.[131]

Chloro(trifluoromethyl)carbene has been generated by the photolysis of the corresponding diazirine at 25 °C.[132] The addition of $F_3C(Cl)C$: to *cis*- and *trans*-but-2-enes takes place stereospecifically but the yields of the corresponding cyclopropanes are low. Chloro(phenoxy)carbene has been obtained similarly on photolysis of diazirine.[17] Cyclopropanes have been obtained in the presence of alkenes in 10–30% yield. Fluoro(methoxy)carbenes have been generated by the thermolysis and photolysis of fluoro(methoxy)-diazirine;[133] in the presence of acrylonitrile and methyl acrylate, the corresponding cyclopropanes were obtained in low yields. The intermediate formation of halogenocarbenes has been postulated in the stereoselective synthesis of 1-halogeno-2-siloxyalkenes:[134]

$$X_3CCHR^2OSiMe_2R^1 \xrightarrow{BuLi} X\ddot{C}CHR^2OSiMe_2R^1 \rightarrow \underset{H}{\overset{X}{}}\!\!\diagup\!\!C{=}C\!\!\diagdown\!\!\overset{OSiMe_2R^1}{R^2}$$

68–96%; X=Cl, Br

In recent years, increased attention has been paid to the study of halogeno(vinyl)carbenes, whose synthetic value is associated with the fact that it is possible to construct with their aid one of the main structural elements of pyrethroids—the vinylcyclopropane fragment. The thermolysis of tetrachlorocyclopropene (> 150 °C) results in the formation of perchlorovinylcarbene,[20,47,135,136] which reacts with alkenes to form the corresponding cyclopropanes (in approximately 60° yield) or is inserted in C–H bonds of heptane and adamantane:



Other halogenovinylcarbenes, namely $Cl_2C{=}CCl\ddot{C}F$, $Cl_2C{=}CH\ddot{C}Cl$, and $Cl_2C{=}CCl\ddot{C}Cl$ obtained by treating the corresponding halogenoalkenes with lithium amides, form halogenovinylcyclopropanes in low yields.[137] The formation of $Me_2C{=}CCl\ddot{C}Cl$ has been postulated in the reaction involving the treatment of 2,2,3-trichloro-1,1-dimethylcyclopropane with MeLi.[138] New (2-chlorovinyl)carbenes have also been obtained by the reaction of $MeClC{=}CHCHCl_2$ and 2-chloro-1-(dichloromethyl)cyclopentene with potassium t-butoxide.[139] The addition of these carbenes to *cis*-but-2-ene takes place entirely stereospecifically. Chloro(2-furyl)- and chloro(2-thienyl)-carbenes have been obtained by treating 2-dichloromethyl-substituted furan and thiophen derivatives with potassium t-butoxide and dibenzo-18-crown-6 ether.[140]

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