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Arynes and Carbenes Derived from Organoelement Compounds

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The literature data on the methods for the synthesis of unstable intermediate species (arynes and carbenes) from organoelement compounds, mainly from *o*- and α-halogeno-derivatives, are surveyed and examined critically. It is shown that the ease of decomposition of the initial compound is determined by the possibility of the formation in the transition state of the coordinate bond between the groups or atoms eliminated and the theoretical proof of this mechanism is given. The bibliography includes 322 references.

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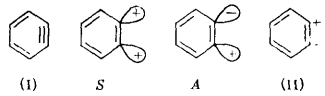
I. INTRODUCTION

The chemistry of the reactive molecules having two electrons and two non-bonding orbitals in one carbon atom (carbenes) or two electrons and two weakly bonding orbitals in neighbouring carbon atoms (arynes, cycloalkynes) has been recently transformed into an independent field of organic chemistry, the development of which has been reflected in a number of monographs[1-6] and reviews[7-9]. Organoelement compounds, which are important and sometimes the only precursors of many of the above unstable species, play an extremely important role in the chemistry of arenes and carbenes.

The aim of this review is to survey the available literature data on the decomposition reactions of organoelement compounds which result in the formation of arynes and carbenes. Since the methods of generation of the unstable species from organic derivatives of alkali metals, magnesium, zinc, and mercury have already been considered in detail in fundamental monographs[2-6] and reviews[7-9], the present review includes only the main achievements in this field, and also the results obtained in recent years (1968–1974). The data on the organic derivatives of other metals are treated in detail. For a more complete understanding of the available results, the review presents the fundamental information about the structures and reactivities of dehydrobenzene (DHB) and carbene.

II. THE STRUCTURE AND REACTIVITY OF DEHYDROBENZENE (DHB)

DHB (I), postulated for the first time by Wittig in 1942[10] as an unstable intermediate in the reaction of fluorobenzene with phenyl-lithium, is the simplest aromatic hydrocarbon, one of the C–C linkages of which is formally a triple bond:



(I) *S* *A* (II)

The steric strain arising following the introduction of a triple bond into the rigid aromatic system of benzene is responsible for such a high reactivity that DHB, like other arynes, is a short-lived intermediate product under the conditions of the usual chemical reactions, the involvement of which in the reaction is usually inferred from various indirect features. However, as a result of the application of special methods to the investigation of unstable species, it has become possible to achieve the direct spectroscopic detection of DHB. Thus the ultraviolet and mass spectra of DHB, recorded using flash photolysis, have now been investigated[11,13], and the infrared spectrum of DHB stabilised in a solid argon matrix has been described[14]. The possibility of the stabilisation of DHB by chemical methods has been demonstrated by synthesising a stable complex with nickel carbonyl[15]. The observed spectroscopic characteristics of DHB agree with the theoretical ideas about structure and thus provide the final evidence for the actual existence of arynes.

Qualitative ideas about the electronic structure of DHB can be readily derived by considering the results of the hypothetical reaction involving the homolytic dehydrogenation of benzene. Evidently, when the H_2 molecule is abstracted from neighbouring carbon atoms in benzene, the residual fragment C_6H_4 must have a pair of degenerate hybrid σ orbitals (σ_1 and σ_2) in which two electrons are accommodated. The interorbital interaction between σ_1 and σ_2 removes the degeneracy, leading to a pair of molecular orbitals (MO), the lower orbital (*S*), of the type $\sigma_1 + \sigma_2$, being symmetrical relative to the C_2 axis and the upper orbital (*A*), of the type $\sigma_1 - \sigma_2$, being antisymmetric. Depending on the relation between the energy of repulsion of the electrons in the *S* orbital and the energy of the promotion of an electron from *S* to *A*, the ground state of DHB can be either the singlet $c_1(S)^2 + c_2(A)^2$ ($c_1 > c_2 \geq 0$) or the triplet $(S)^1(A)^1$. Naturally, when only qualitative hypotheses are used, it is impossible to assign correctly the ground and first excited states, although one must bear in mind that, for orbitals of the type $\sigma_1 + \sigma_2$, the electron correlation energy is small (≤ 1 eV) and the splitting between the *S* and *A* levels is considerable, despite the rigidity of the ring. On the other hand, it is already clear from the above discussion that the structure of the dipolar ion (II), frequently discussed when the reactivity of DHB is described, cannot correspond either to the ground or to the first excited state of the molecule.

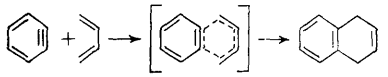
Theoretical calculations on DHB using modern quantum-chemical methods have shown that the molecule has a singlet ground state. Thus, according to calculations based on the extended Hückel method (EHM),[16] the energy of the singlet–triplet splitting (E_{ST}) is 35 kcal mole^{-1} for the DHB molecule, the skeleton of which has the geometry of the benzene molecule. The use for the calculation on the DHB molecule of the semi-empirical SCF INDO/2 method, assuming the same geometry, led accordingly to a lower value of E_{ST} (12.5 kcal mole^{-1}), although a somewhat higher value (20 kcal mole^{-1}) has been postulated for the real molecule[17]. Calculation on the molecule with the same non-equilibrium geometry by the semiempirical LCAO-MO SCF method led to E_{ST} = 17 ± 5 kcal mole^{-1} and the calculated parameters of the ultraviolet spectrum obtained in the same study[18] agreed satisfactorily with the experimental data[12].

The optimum geometrical parameters of the DHB molecule have been calculated by the MINDO/2[19] and MINDO/3 methods taking into account the configuration interaction[20]. According to these calculations, the molecule has the shape of an irregular hexagon with a markedly shortened distance between the $C_{(1)}$ and $C_{(2)}$ atoms; the bond lengths calculated by the two methods are in satisfactory agreement: r_{1-2} = 1.256, r_{2-3} = 1.344, r_{3-4} = 1.399, and r_{4-5} = 1.402 Å in the first set[19] and r_{1-2} = 1.291, r_{2-3} = 1.384, r_{3-4} = 1.417, and r_{4-5} = 1.419 Å in the second set[20]. One should note that the heat of formation of DHB (114.3 kcal mole^{-1}),[20] calculated by the most effective of the modern semiempirical methods (SCF MINDO/3), agrees extremely well with the experimental value 118 ± 5 kcal mole^{-1},[21] which suggests that the geometrical and energetic parameters found for the molecule by Dewar and Li[20] (E_{ST} = 12.4 kcal mole^{-1}, ionisation potential of 8.5 eV) are close to the real values. The low value of E_{ST} is indicated by the extremely rapid conversion of the triplet DHB molecule into the singlet molecule[22].

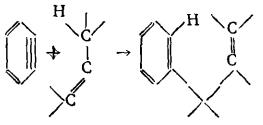
Thus, according to quantum-chemical calculations, the DHB molecule, which is in the singlet ground state, is characterised by a high energy of the highest occupied molecular orbital (HOMO), which is unique for hydrocarbons, and a low energy of the lowest vacant molecular orbitals (LVMO), the boundary orbitals being centred between the $C_{(1)}$ and $C_{(2)}$ atoms and being formed from weakly overlapping σ orbitals of the two atoms. As a consequence of this, the molecule should exhibit a high electrophilic reactivity in relation to unsaturated systems and also an ability to enter into reactions characteristic of both singlet biradicals and unsaturated compounds.

The available data on the reactivity of DHB are fully consistent with this conclusion: it readily reacts as a dienophile in the Diels–Alder reaction, enters into many other cycloaddition reactions, and is capable of being inserted into single C–H, C–metal, and other bonds[2,3].

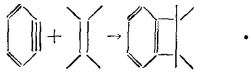
The mechanism of the interaction of DHB with planar conjugated *cis*-dienes is consistent with a concerted 2*s* + 4*s* cycloaddition reaction[23-25]:



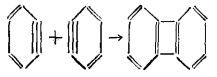
The reaction involving the 1,4-cycloaddition of DHB to aromatic systems proceeds via the same mechanism[26]. The above reactions with non-planar cyclic polyenes, for which the 2*s* + 4*s* cycloaddition reactions are not so energetically favourable, compete with the so called ene addition[27,28], which is also characteristic of the reactions of DHB with olefins:



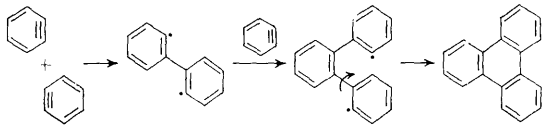
The simultaneous formation of benzocyclobutene is also usually observed under these conditions:



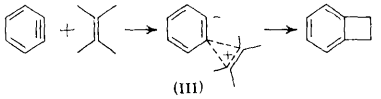
Judging from the dependence of its stereoselectivity on the nature of the olefin[24,25,29], this reaction can proceed as concerted 2*s* + 2*s* cycloaddition when E_{ST} for the transition state is small[30]. In view of the evidently low value of E_{ST} for the transition state, this mechanism should also operate in the dimerisation of DHB to biphenylene, which is usually formed as the main product in the gas-phase generation of DHB[2]:



The formation of terphenylene—another product of these reactions—proceeds either via the concerted 2*s* + 2*s* + 2*s* cycloaddition or, more probably, via a stepwise biradical process due to the transoid approach of the reactants:

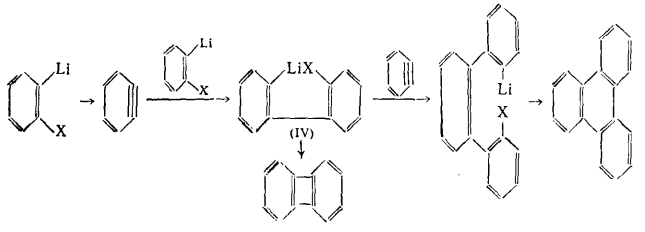


Analogous cyclodimerisation and cyclotrimerisation reactions are characteristic of cycloalkynes[31,32], and higher cycloalka-1,2-dienes[34], which also have a singlet ground state[35]. In the absence of acceptors, cyclohexa-1,2-diene in the triplet ground state[35] forms a tetramer[36]. According to calculated data[37], the addition of DHB to ethylene can proceed with the intermediate formation of a dipolar phenonium ion (III):



(III)

During its generation from organometallic compounds, DHB is readily inserted in the C–metal bond of the initial compound, which also leads to biphenylene and terphenylene, but naturally via a different pathway:



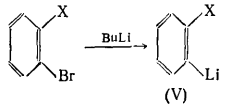
(IV)

In contrast to the majority of thermolytic gas-phase reactions, the main product here is usually terphenylene,

while biphenylene is formed in trace amounts. Since the cyclisation of compound (IV) requires the flattening of the biphenyl molecule, the yield of biphenylene under these conditions may be greatly increased by carrying out the reaction in the presence of aromatic hydrocarbons or adsorbents promoting such flattening[39].

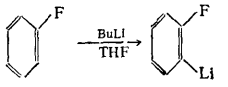
III. ARYNES DERIVED FROM ORGANOMETALLIC COMPOUNDS

Among the organometallic precursors of DHB and its substituted derivatives, *o*-halogenolithiobenzenes (V, X = F, Cl, or Br) have been most thoroughly investigated. The first representatives of compounds of this class were synthesised as early as 1956, by the low-temperature reaction of aliphatic organolithium compounds with the corresponding *o*-dihalogenobenzenes in ether or tetrahydrofuran (THF)[40]:

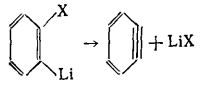


(V)

A large number of organolithium aryne precursors, the information about the thermal stability of which is presented in Table 1, have now been synthesised. Together with the exchange of a halogen atom for lithium, the H-metallation reaction is used in the synthesis of compound (V), for example[2]:



Compounds (V, X = F, Cl, or Br) without other substituents are labile, exist in solution only at low temperatures, and readily split off LiX with formation of DHB:



It follows from cryoscopic and NMR data[41-44] that in ether–hydrocarbon solutions *o*-fluorophenyl-lithium is a tetrameric tetraetherate, $(o\text{-}FC_6H_4Li)_4(R_2O)_4$, whose structure is analogous to that of the etherates of aliphatic organolithium compounds[45]. According to the results of differential thermal analysis, the stability of this compound, determined like that of other compounds (V), by the decomposition temperature T_d in solution, depends on the nature of the ether R_2O (Table 1), while in media without ethers, the compounds decompose at the instant of their formation[41,44]. Judging from the ^1H and ^{19}F NMR data, the carbon–lithium bond in the *o*-fluorolithiobenzene molecule is not appreciably polarised under the influence of the neighbouring fluorine atom, although both atoms [lithium and fluorine?] interact appreciably through space[39]. The influence of the lithium atom on the mobility of halogen atoms linked to the benzene ring under conditions ensuring the stability of halogenolithiobenzenes is in its turn apparently also small, since in some cases polylithio-compounds can be obtained by treatment with an excess of a lithium alkyl under extremely mild conditions, for example[46,47,48]:

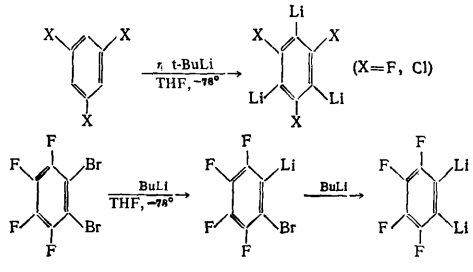
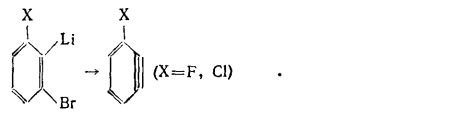


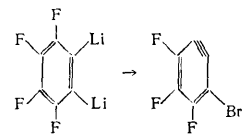
Table 1. Thermal stabilities of organolithium aryne precursors.

Compound	Solvent	Stability characteristic	References
1	2	3	4
o-Fluorolithiobenzene	acyclic ethers	$T_d = -48° \text{--} -50°C$	41, 42
	cyclic ethers	$T_d = -19° \text{--} -21°C$	41, 42
o-Chlorolithiobenzene	acyclic ethers	$T_d = -70° \text{--} -73°C$	41, 42
	cyclic ethers	$T_d = -50° \text{--} -52°C$	41, 42
o-Bromolithiobenzene	acyclic ethers	$T_d = -83° \text{--} -85°C$	41, 42
	cyclic ethers	$T_d = -73° \text{--} -75°C$	41, 42
2,6-Difluorophenyl-lithium	THF	stable at −65°C	54
2,4,6-Trifluorophenyl-lithium	THF	stable at −70°C	47
3,4,5,6-Tetrafluorophenyl-lithium	THF, Et_2O	stable at −55°C	55
2,4,5,6-Tetrafluorophenyl-lithium	Et_2O	stable at −75°C	56
2,3,5,6-Tetrafluorophenyl-lithium	THF	stable at −55°C	55
Pentafluorophenyl-lithium	THF	polymerises at 0°C	57
Pentafluorophenyl-lithium	Et_2O	decomposes at 15°C, partly stable at 20°C	51
2-Fluoro-1-lithionaphthalene	THF	$T_d = -30°C$	58
Octafluoro-4,4′-dilithio-biphenyl	THF, Et_2O	decomposes at −5° –0°	59
Octafluoro-2,2′-dilithio-biphenyl	Et_2O	decomposes at 0°C	60
Pentafluorophenylpenta-fluoro-4-lithiophenyl ether	THF	decomposes via the aryne mechanism at −30°C	61
4,4′-difluoro-3,3′-dilithio-biphenyl	THF, Et_2O	stable at −78°C	62
2-Bromo-3,4,5,6-tetra-fluorophenyl-lithium	Et_2O	decomposes in 8 h at 0°C	48
2,4,6-Trifluoro-1,3-dilithio-benzene	THF	stable at −78°C	47
Tetrafluoro-1,2-dilithio-benzene	THF, Et_2O	stable at $T \leqslant -55°C$	55
Tetrafluoro-1,4-dilithio-benzene	THF, Et_2O	stable at $T \leqslant -65°C$	54
Tetrafluoro-1,3-dilithio-benzene	Et_2O	stable at $T \leqslant -75°C$	56
3,5-Dichloro-2,4,6-trifluoro-phenyl-lithium	Et_2O	stable at $T \leqslant -75°C$	56
5-Chloro-2,4,6-trifluoro-1,3-dilithiobenzene	Et_2O	stable at $T \leqslant -75°C$	56
3-Chloro-2,4,5,6-tetrafluoro-phenyl-lithium	Et_2O	stable at $T \leqslant -75°C$	56
2,4,6-Trifluoro-1,3-trilithio-benzene	THF	$T_d \approx -60°C$	47
2,4,6-Trichlorophenyl-lithium	THF	stable at −65°C	46
2,3,5,6-Tetrachlorophenyl-lithium	Et_2O	stable at −10°C	63
2,3,4,5-Tetrachlorophenyl-lithium	Et_2O	stable at −20°C	63
Pentachlorophenyl-lithium	Et_2O	decomposes slowly in the presence of furan at ~20°C;	52
ditto		stable in crystalline state at 20°C in air	53
Nonachlorolithiobiphenyl	THF	stable at −30°C	64
Octachlorodilithiobiphenyl	THF	stable at −30°C	64
2,4,6-Trichloro-1,3-dilithio-benzene	THF	stable at −65°C	46
2,4,6-Trichloro-1,3,5-trilithio-benzene	THF	stable at −65°C	46
Tetrachloro-4-lithiopyridine	Et_2O	stable at ~ 20°C	65
2,3,6-Trichloro-4-lithio-pyridine	Et_2O	stable at −20°C	63
Pentabromophenyl-lithium	Et_2O	stable at −15°C	52
	benzene	stable at 80°C	
2′-Bromo-2-lithiobiphenyl	Et_2O	stable at 20°C	53

In the majority of known cases, the ease of decomposition of compounds (V) with formation of arynes increases with decrease of the C–X bond energy, so that the decomposition temperatures of compounds of the type *o*-XC_6H_4Li decrease in the following series of X : F > Cl > Br. The same relation has been observed for 2,6-dihalogenolithiobenzenes with different halogen atoms[2]:

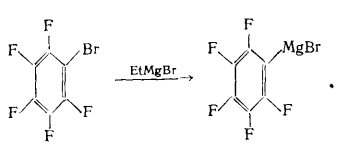


However, the accumulation of fluorine atoms in the molecule of the initial polyhalogenolithiobenzene alters the mode of elimination of LiX. For example, the only product of the decomposition of 2-bromo-3,4,5,6-tetrafluorophenyl-lithium is bromotrifluorodehydrobenzene (VI),[49] which may be attributed to thermodynamic control of the reaction[50,51]:

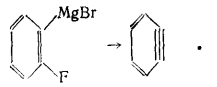


An interesting feature of pentahalogenolithiobenzenes, usually obtained by the reaction of lithium alkyls with penta- or hexa-halogenobenzenes, is their high thermal stability, compared with *o*-halogenolithiobenzenes (V), which is usually attributed[2] to stabilisation of the corresponding phenyl anions by the halogen atoms. However, comparison of the decomposition temperatures of C_6X_5Li and the corresponding compounds (V) shows that this explanation is not exhaustive. Thus pentafluorophenyl-lithium, the anion of which should be the most stable species of this kind, decomposes slowly in an ethereal medium at 0°C, i.e. at a temperature only slightly higher than for *o*-fluorophenyl-lithium (T_d = −20°C in THF). On the other hand, pentachlorophenyl-lithium is entirely stable under the usual conditions and can be stored at 20°C and even higher temperatures in the crystalline state, while *o*-chlorophenyl-lithium decomposes in THF at −50°C.[41,53] A similar difference between stabilities has also been noted for the corresponding bromo-derivatives (T_d = 0°C for pentabromophenyl-lithium compared with −75°C for *o*-bromophenyl-lithium in THF).[52] It is noteworthy that the decomposition of pentahalogeno-derivatives of phenyl-lithium with formation of arynes is appreciably complicated by reactions of the S_N2 type, which are much less common for monohalogenolithiobenzenes[2].

Together with halogeno-derivatives of organolithium compounds, the analogous *o*-halogenophenylmagnesium halides behave as common organometallic precursors of arynes. Compounds of this type are obtained either by the reaction of dihalogenobenzenes with metallic magnesium in ether or THF or by an exchange interaction between aromatic halogeno-derivatives and aliphatic organomagnesium compounds[66,67]:



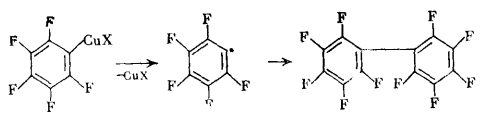
Halogeno-derivatives of aromatic organomagnesium compounds are more stable than the corresponding organolithium compounds[68,69] and in most cases decompose at a moderate rate only at the boiling point of the solvent (ether or THF):



Like the analogous lithium compounds, pentahalogenophenylmagnesium halides are more stable than the corresponding monohalogenophenyl derivatives. However, the main pathway in the reactions of these compounds in ethereal media involves intermolecular reactions of the S_N2 type, as a result of which they are widely used to introduce pentahalogenophenyl groups into various compounds. The aryne decomposition of pentahalogenophenyl magnesium halides is achieved in a hydrocarbon medium at extremely high temperatures (approximately 200°C)[52,70].

o-Iodophenylmercury iodide or bis-2-iodophenylmercury decompose at approximately 200°C, which leads to DHB according to Hoffmann[2]. On the other hand, bis-pentachlorophenyl- and bis-pentafluorophenyl-mercury are stable at higher temperatures[2] and even bis-(2-bromo-3,4,5,6-tetrafluorophenyl)mercury enters into various reactions at 230°C without undergoing the aryne decomposition[71].

Numerous pentahalogenophenyl derivatives of many other elements (Zn, Cu, Ag, B, Al, In, Tl, Si, Ge, Ti, Co, Fe) have been synthesised from pentahalogeno-derivatives of lithium and magnesium, but the thermolysis products of these compounds were not investigated, although in most of the known cases they exhibit a thermal stability characteristic of the analogous phenyl derivatives or higher[2,72], which apparently indicates their low tendency to undergo the aryne decomposition. For the less stable halogenophenyl compounds of copper, silver, cobalt, and titanium, the most probable thermolytic pathway is homolytic rupture of the carbon–metal bond with formation of free radicals[33,73–76], for example:



Pentafluorophenyl derivatives of boron, aluminium, and indium, among which $(C_6F_5)_3B$ and $(C_6F_5)In$ are fully stable and can be readily synthesised by the exchange reaction between pentafluorophenyl-lithium and the corresponding halides, possess interesting properties[77]. On the other hand, trispentafluorophenylaluminium can only be obtained in the form of the etherate, which decomposes explosively when any attempt is made to remove the ether even at a relatively low temperature (approximately 20°C). The attempt to synthesise $(C_6F_5)_3Al$ in an ether-free medium leads to the same result and the product of the decomposition of this compound is presumably the corresponding aryne.

On heating $(C_6F_5)_2TlBr$ with various elements, pentafluorophenyl derivatives of the type $(C_6F_5)_nM$ (where M = S, Se, Te, P, As, Sb, Sn, Zn, or Cd) were obtained, being fully stable at approximately 200°C.[78]

$W(C_6F_5)_5$[79] as well as compounds of the type C_6F_5HgX (where X represents iron, manganese, and molybdenum carbonyls) are also resistant to aryne decomposition[80].

IV. THE STRUCTURE AND REACTIVITY OF CARBENES

Like other molecules containing carbon atoms with an incomplete shell, the carbenes CRR′ exhibit an enhanced reactivity and are involved in chemical reactions as short-lived intermediates. Nevertheless, the use of special physical and physicochemical methods has now made it possible not only to demonstrate reliably the involvement of carbenes in many reactions (particularly in the decomposition of halogeno-derivatives of organometallic compounds[81,82]) but also to determine the thermodynamic and structural parameters of many of them[83,84].

Since the central atom of the carbene has two non-bonding orbitals accommodating two electrons, the CRR′ molecule may exist in singlet or triplet states characterised by parallel and antiparallel spins of the free electrons. The spin state of the carbene determines to a large extent its reactivity, since compounds in the triplet state have a reactivity close to that of free radicals, and those in the singlet state can exhibit properties of both compounds with a free electron pair as well as compounds having a vacant orbital, i.e. they can behave as nucleophiles or electrophiles, depending on the nature of the substituents R and R′. For this reason, the main theoretical problem of the chemistry of carbenes is the relation between the structural parameters and the spin state of the molecule.

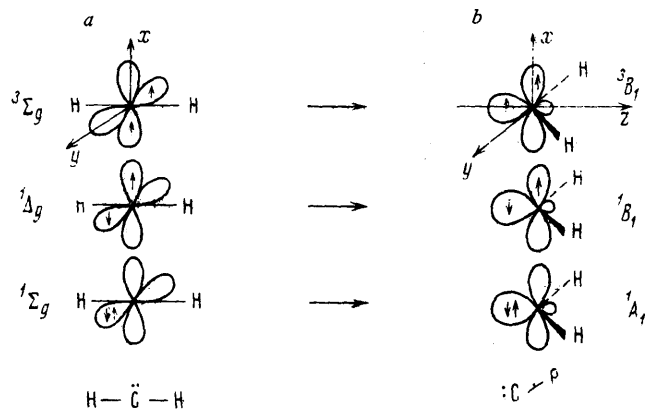


Figure 1. The spin states of methylene: *a*) linear form; *b*) bent form.

In broad outline, this problem may be examined even in relation to the simplest carbene—methylene[85]. Evidently the carbon atom of the linear CH_2 molecule can have two *sp* hybrid orbitals involved in the formation of C–H bonds and two non-bonding *p* orbitals (p_x and p_y) accommodating two electrons. According to the Pauli principle, the possible states of this molecule ($D\infty h$ symmetry point group) should be arranged in the following sequence in terms of their energies: $^3\Sigma_g < {}^1\Delta_g < {}^1\Sigma_g$, so that the linear CH_2 molecule should have a triplet ground state. A decrease of the H–C–H valence angle, i.e. the bending of the molecule, for example in the *yz* plane, as shown in Fig. 1, removes the degeneracy of the p_x and p_y orbitals, since the former, being symmetrical relative to the *yz* plane, remains a pure *p* orbital under these conditions, while the latter acquires some *s* character, being converted into a hybrid σ orbital. This change in the shape of the molecule alters its symmetry point group to C_{2v} with the possible states $^3B_1$, $^1B_1$, and $^1A_1$. Evidently, on transition from the $^3\Sigma_g$ and $^1\Delta_g$ states to the corresponding $^3B_1$ and $^1B_1$ states, the energy of one of the free electrons is reduced. When this effect is greater than the decrease of the energy of the C–H bond owing to the reduction of the amount of *s* character of the corresponding hybrid atomic orbitals, the $^3B_1$ and $^1B_1$ states will be energetically more favourable than the $^3\Sigma_g$ and $^1\Delta_g$ states respectively. The molecule will therefore "strive" to increase the valence angle until the associated energy gain is compensated by the energy of repulsion between the hydrogen atoms. Since the analogous transition between the $^1\Sigma_g$ and $^1A_1$ singlet states is associated with approximately twice as great an energy gain as the transition between the first two states, presumably the equilibrium valence angle in the molecule in the $^1A_1$ state should be smaller than in the molecule in the $^3B_1$ or $^1B_1$ state.

Thus, general considerations arising from valence theory lead to the conclusion that the methylene molecule must have a triplet ground state in which it is bent and an excited singlet state with the same or smaller valence angle. On passing from methylene to other carbenes, which naturally have more bulky substituents, one must expect an increase of the valence angles in any state of the molecule. It is also evident that the interaction of the occupied orbitals of the substituents R and R′ of the CRR′ molecule with the p_x orbital of the central atom should lead to a specific stabilisation of the $^1A_1$ singlet state (or another state of the σ^2 type), and the existence of carbenes in a singlet ground state should therefore be caused by a fairly strong interaction of this type[86].

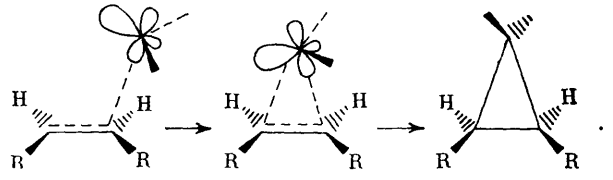
The results of many experimental[5,84] and theoretical[5,85–88] studies devoted to the problem of the structure of carbenes are in full agreement with these considerations. It has now been established that methylene and its alkyl alkenyl, alkynyl, and aryl derivatives have triplet ground states and singlet first excited states. On the other hand, singlet ground and triplet first excited states have been found for dihalogenocarbenes, the maximum value of *E*ST (39–47 kcal mole^{-1}[88,89]) corresponding to the CF_2 molecule, where the extent of the interaction of the *p* electrons of the substituents and the p_x orbital of the carbon atom is greatest. In all known cases, the experimental R–C–R′ valence angles vary in the range 130–180° for triplet molecules and 100–115° for singlet molecules[5,84]. In particular, the formation of singlet dichlorocarbene with a Cl–C–Cl angle of approximately 106° in the decomposition of $LiCCl_3$[81] and $PhHgCCl_3$[82] has been demonstrated by infrared spectroscopy using the technique of matrix isolation of unstable molecules.

The majority of the known methods for the generation of carbenes are based on the decomposition of stable initial molecules in the ground electronic state. In those cases where the decomposition of the precursor is a single-stage reaction, the carbene is therefore formed in a singlet state owing to spin conservation regardless of whether it is the ground or an excited state. Thus the reactivity of carbenes in the triplet ground state is determined to a large extent by the possibility of a singlet–triplet transition under the conditions of their generation—in the absence of such transition, they react in an excited singlet state.

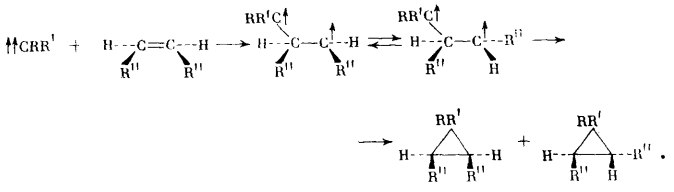
Like arynes, singlet carbenes have a low-lying LCMO. Accordingly, the reactivity of singlet carbenes is to some extent analogous to that of arynes, which was discussed

above: they are active electrophiles in relation to unsaturated organic compounds with which they readily form adducts—compounds of the cyclopropane or cyclopropene series. Furthermore, a characteristic feature of carbenes as a whole is their ability to undergo reactions involving insertion in various single bonds and also dimerisation to the corresponding olefins.

The reaction of carbenes which is most important in practice—addition to the double bonds of olefins—is stereospecific for singlet CRR′ with retention of the configuration of the initial olefin in the cyclopropane formed. Such a reaction, which is undoubtedly a single-stage process, is allowed by the orbital symmetry conservation rules in the form of a non-linear cheletropic process[90]. According to calculations[91-93], a reaction of this kind begins with electrophilic attack by the p_X orbital in the carbene on one of the carbon atoms of the π-system of the olefin and further mutual approach of the reactants is accompanied by the rotation of the carbene fragment about the axis passing through its central carbon atom at right angles to the plane of the three-membered ring being formed:

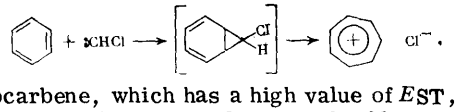


In contrast to singlet carbenes, triplet carbenes add to multiple bonds in the course of the two-stage reaction involving the intermediate formation of a triplet trimethylene biradical. The cyclisation of the latter to the corresponding cyclopropane is caused by the possibility of spin inversion and, according to Skell's postulate[94], such a biradical has a lifetime sufficiently long for the attainment of the conformational equilibrium, which entails the loss of stereoselectivity:



Thus Skell's postulate makes it possible to determine the spin state of the reacting carbene from the stereochemical result of the conversion of olefins into cyclopropanes, which is widely used in the study of carbene reactions.

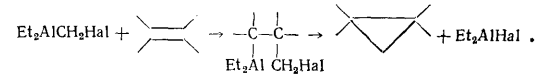
Since carbenes manifest properties of electrophiles in cycloaddition to unsaturated systems, their reactivity is determined by the energy of the LUMO and is greater the lower the energy level of this orbital. Accordingly, carbenes whose singlet state has been stabilised as a result of the raising of the LUMO level show the least reactivity in these reactions. Thus dichlorocarbene is incapable of adding to benzene[95], although this reaction does proceed with methylene[96] and monochlorocarbene[95,97,98], for example:



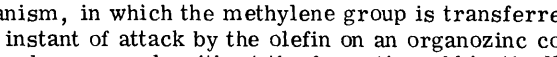
Difluorocarbene, which has a high value of EST, shows altogether little tendency to undergo cycloaddition reactions.

Like cycloaddition to olefins, the dimerisation of singlet carbenes begins, according to calculations[99], with electrophilic attack by the p_X orbital of one :CRR′ molecule on the σ orbital of another, as a result of which further mutual approach of the molecules involves the rotation of at least one of them. Further, one may expect that both reactions (dimerisation and conversion of olefins into cyclopropanes) proceed via the shortest pathway as a result of configuration interaction in the transition state[30], because the values of EST for the majority of singlet carbenes are small (for example 1–1.5 eV or $:CCl_2$).[86]

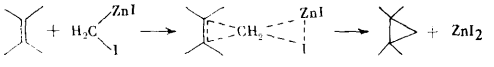
However, the above considerations concerning the mechanism of the formation of cyclopropanes and olefins are by no means applicable to all reactions in which labile organometallic compounds are used as carbene precursors. Thus organoaluminium compounds of the type Et_2AlCH_2Hal exhibit, according to Hoberg's data[100], a greater tendency towards the addition of olefins to the C–Al bond than towards the elimination of methylene, as a result of which the cyclopropanes are formed in this case via a γ-elimination mechanism:



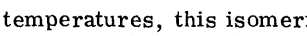
In the decomposition of certain halogenolithiomethanes, for example $LiCH_2Cl$ or $LiCHCl_2$,[101] the main reaction pathway appears to be the insertion of the carbene formed in the C–Li bond, occurring within the cage formed by the association complex of the initial organolithium compound[39,102,103]. As a consequence of this, the reaction product is a formal carbene dimer formed via β-elimination, for example:



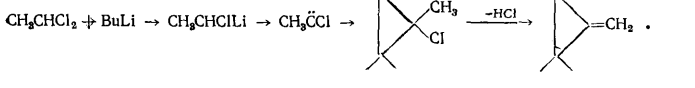
According to Blanchard and Simmons[104], the conversion of olefins into cyclopropanes via the Simmons–Smith mechanism, in which the methylene group is transferred at the instant of attack by the olefin on an organozinc compound, also proceeds without the formation of kinetically independent methylene:



The presence of a low-lying LUMO and a high HOMO determines the ability of carbenes, containing more than one carbon atom, to undergo various intramolecular rearrangements. The commonest reaction of this type is the so called carbene–olefin isomerisation, which is one of the examples of symmetry-allowed sigmatropic rearrangements[90,105]†:

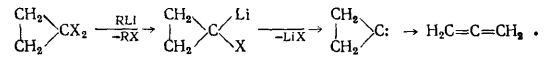


At low temperatures, this isomerisation can be avoided in certain cases. The recently proposed method for synthesising methylenecyclopropanes is in fact based on this finding[106]:

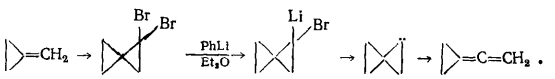


† According to calculations by the MINDO/2 method[109], the isomerisation of ethylidene to ethylene proceeds without activation energy.

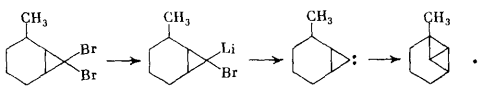
The carbene–olefin isomerisation of cyclopropylidene and a wide variety of its substituted derivatives proceed with ring opening, which results in the formation of the corresponding allenes[107]:



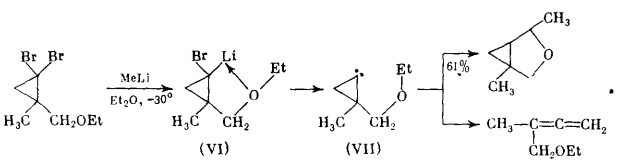
In view of the availability of *gem*-dihalogenocyclopropanes, this reaction constitutes a convenient general method for the synthesis of allenes, many of which cannot be obtained by other methods, for example[108]:



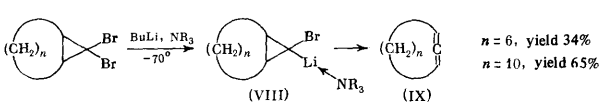
According to calculated data[110], the rearrangement of cyclopropylidenes to allene proceeds with a somewhat higher activation energy than the addition of the carbene to the double bond. Accordingly, in certain cases it is possible to observe also carbene reactions of cyclopropylidenes, for example the addition to olefins with formation of the corresponding spiropentanes[111]. Norcarylidene, which is formed by the reaction of 7,7-dibromonorcarane with metallic lithium in THF between −20° and −60°C, reacts with the solvent without a rearrangement, giving rise to 7-(α-tetrahydrofuryl)norcarane[112]. It is interesting to note that the analogous reaction of 3-methylnorcarylidene leads to a bicyclobutane derivative[113], with a 90% yield:



The formation of substituted bicyclo[1,1,0] butanes, which competes with the cyclopropylidene–allene isomerisation, has been noted also for certain di- and tetra-alkylcyclopropylidenes[114,115], the ratio of the bicyclic and allene reaction products being determined by the positions and nature of the substituents. The preferential insertion of the carbene centre of cyclopropylidene in the C–H bond has also been noted for compound (VII), where the proximity of the reaction centres is apparently ensured by the intramolecular coordinate bond Li ← O in the organometallic precursor (VI)[116]:

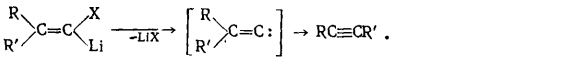


Accordingly, the use in this type of reaction of an optically active amine, (-)-sparteine, which forms a chiral complex with the intermediate bromolithio-derivative (VIII), leads to optically active cyclic allenes (IX), albeit with a low optical purity[117]:



It evidently follows from these data that the cyclopropylidene generated from a halogeno-derivative of an organolithium precursor rearranges at the instant of formation.

Another interesting example of the isomerisation of a carbene, synchronised with the decomposition of the organometallic precursor, is the Frisch–Buttenberg–Wieche rearrangement:



Judging from the process selectivity (only the aryl or cyclopropyl group R′ in the *trans*-position relative to the halogen atom migrates[118,119]), the rearrangement apparently takes place at the instant of the decomposition of the halogeno-derivative of the organometallic compound, which is accelerated by the interaction of the π-orbital of the migrating group with the σ*-orbital of the C–X group.

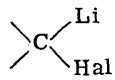
V. CARBENES DERIVED FROM ORGANOMETALLIC COMPOUNDS

1. Halogenoalkyl Derivatives of Alkali Metals

Aliphatic organometallic compounds containing in the α-position a halogen atom or another group tending to be split off in the form of an anion exhibit in many instances a capacity for thermal α-elimination with formation of carbenes:

$$RR'CMX \rightarrow RR'C: + MX .$$

The ease of this reaction is determined mainly by the nature of the eliminated M and X groups. In particular, many compounds of this type, capable of generating carbenes at low or moderate temperatures (between −100° and +100°C), which are particularly convenient for liquid phase reactions, are known. The comparative availability of numerous compounds of the type **RR′CMX** together with the ease of their decomposition make them important and widely used sources of carbenes.

Halogenolithiomethanes and related compounds containing the  group are the most thoroughly investigated compounds of this type. Halogenomethyl derivatives of lithium are usually obtained by treating the corresponding halogenomethanes with lithium alkyls or phenyl-lithium at low temperatures. The ease of exchange of the substituents at the carbon atom for lithium in an ethereal medium diminishes in the sequence I > Br > H > Cl.[120,121] It follows from the observation of the effects of the chemically induced polarisation of nuclei observed in NMR spectra that the exchange reaction in lithium alkyl–alkyl halide systems[122,123] proceeds at least partially with intermediate formation of free radicals:

$$RX + R'Li \rightarrow R^{\cdot} + R'^{\cdot} + LiX$$
$$R^{\cdot} + R'Li \rightarrow RLi + R'^{\cdot} \text{ etc.}$$

Exchange reactions are catalysed by Lewis bases forming complexes with organolithium compounds (ethers and amines)[45,124] and in some cases the nature of the solvent influences also the mode of reaction. Thus, when methyl-lithium is allowed to react with benzylidene bromide in ether, the bromine atom is substituted and the product is α-lithiobenzyl bromide, which decomposes subsequently with formation of phenylcarbene. However, the analogous reaction in THF proceeds as H-metallation,

leading to α-lithiobenzylidene bromide and further to bromophenylcarbene[125,126]:

$$PhCHBr_2 \begin{cases} \xrightarrow[Et_2O]{} PhCHLiBr \xrightarrow[-LiBr]{} :CHPh \\ \xrightarrow[THF]{} PhCLiBr_2 \xrightarrow[-LiBr]{} :CBrPh \end{cases}.$$

Benzylidene chloride is metallated by methyl-lithium in ether preferentially at the hydrogen atom[127]:

$$PhCHCl_2 \xrightarrow{MeLi} PhCLiCl_2 \xrightarrow[-LiCl]{} :CClPh .$$

A mixture of similar amounts of $LiCBr_3$ and $LiCHBr_2$ is formed in an analogous manner as a result of the reaction of butyl-lithium with bromoform in THF[128,129], whereas in a hydrocarbon medium the exchange of bromine for lithium takes place exclusively[129]:

$$CHBr_3 + BuLi \begin{cases} \xrightarrow[-BuH]{} LiCBr_3 \xrightarrow[-LiBr]{} :CBr_2 , \\ \xrightarrow[-BuBr]{} LiCHBr_2 \xrightarrow[-LiBr]{} :CHBr , \end{cases}$$

$$CHBr_3 + BuLi \xrightarrow[-BuBr]{hexane} LiCHBr_2 \xrightarrow[-LiBr]{} :CHBr .$$

The analogous reaction of chloroform in ether leads to $LiCCl_3$,[130] the decomposition of which results in the formation of dichlorocarbene, and, when the reaction is carried out in a hydrocarbon medium, the product is a mixture of $LiCCl_3$ and $LiCHCl_2$.[129]

Under the influence of lithium alkyls, dihalogenomethanes CH_2X_2 (X = Cl, Br, or I) in hydrocarbons exchange only halogen atoms for lithium[102,103,131], with subsequent formation of methylene. However, in an ethereal medium, CH_2Cl_2 undergoes exclusively H-metallation, being converted into $LiCHCl_2$—a precursor of monochlorcarbene[132,133]:

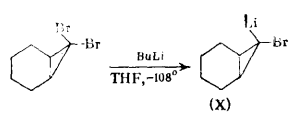
$$CH_2Cl_2 + BuLi \xrightarrow[-BuH]{Et_2O} LiCHCl_2 \xrightarrow[-LiCl]{} :CHCl .$$

This change in the mode of metallation on passing from a hydrocarbon medium to an ethereal medium can be explained[129] by a weakening of the C–H bond owing to the formation of complexes of the type $X_3C...H...OR_2$.

The reaction of phenyl-lithium and its substituted derivatives with CH_2Cl_2 in ether, which also leads to the intermediate formation of monochlorcarbene, constitutes the basis of a convenient method for the generation of arylcarbenes[134]:

$$CH_2Cl_2 + ArLi \xrightarrow[-ArH]{} LiCHCl_2 \xrightarrow[-LiCl]{} HClC: \xrightarrow{ArLi} ArCHLiCl \rightarrow ArHC: .$$

Bicyclic *gem*-dibromo-derivatives, namely 7,7-dibromonorcarane, 7,7-dibromo-2-oxanorcarane, and related compounds, exchange the *endo*-halogen preferentially for lithium in the reaction with lithium alkyls[135]:



(X)

On the other hand, 7,7-dichloronorcarane forms under analogous conditions (THF, −115°C) a mixture of *endo*- and *exo*-lithio-derivatives with the *exo*-isomer predominating appreciably[136].

A simple general method for the generation of halogenocarbenes is based on the reactions of di-, tri-, and tetra-halogenomethanes and similar compounds with metallic lithium or sodium in THF[137] at temperatures between −40° and +40°C, i.e. under conditions where the majority of α-halogenolithiomethanes are unstable:

$$RR'CXX' \xrightarrow[THF]{Li} RR'CLiX \xrightarrow[-LiX]{} RR'C: \rightarrow \text{(norcarane)}(R)(R') ,$$

where X and X′ are halogens and R,R′ = H, halogen, aryl, alkyl, etc.

It has been shown[127] that $PhCHCl_2$ reacts with lithium in THF even at −90°C; heating of the reaction mixture in the presence of cyclohexene leads to a high yield of 7-chloro-7-phenylnorcarane, which undoubtedly demonstrates the intermediate involvement of $PhCLiCl_2$. It is interesting to note that CH_2Cl_2, $CHCl_3$, $PhCHCl_2$, and $CHBr_3$ react with lithium only via the hydrogen atom under these conditions, whereas the reaction with CH_2Br_2 involves bromine[112,138]. In contrast to lithium alkyls and metallic lithium, lithium amides are capable of exchanging lithium only for hydrogen atoms in polyhalogenomethanes. Thus, when dibromomethane is treated with lithium di-isopropylamide in THF, the following reaction takes place unambiguously[139]:

$$CH_2Br_2 + iso\text{-}Pr_2NLi \rightarrow LiCHBr_2 + iso\text{-}Pr_2NH .$$

Such selectivity is evidently proof that the reaction is thermodynamically controlled, since the exchange of the halogen should have led in this case to labile *N*-halogenoamines.

The halogenolithiomethanes formed via H- or X-metallation reactions at low temperatures (at approximately −100°C) in an ethereal medium undergo intermolecular reactions involving not only the C–Li bond but also the exchange of halogen atoms[140]:

$$LiCBr_3 + LiCCl_3 \rightarrow LiCBrCl_2 + LiCBr_2Cl .$$

The exchange reactions of halogenolithiomethanes with lithium halides have also been reported[141]. Numerous halogenolithiomethanes and their substituted derivatives have now been synthesised by the methods examined above (Table 2).

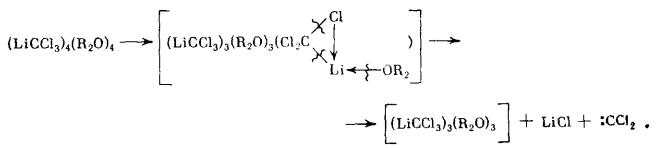
Table 2. Thermal stabilities of halogenolithiomethanes.

Compound	Solvent*	T_d, °C	References
$LiCF_3$	Et_2O	−75 to −50	142
$LiCH_2Cl$	THF	−110	101
$LiCHCl_2$	THF	−30	143
	Et_2O	−100	133
$LiCCl_3$	THF and other cyclic ethers	−65	42, 130
	Et_2O and other acyclic ethers	−84 to −88	42
	monoglyme, TMEDA	−75	42
$LiCHBr_2$	THF	−73	144
$LiCBr_3$	THF	−77	144
$LiCH_2I$	THF	−110	145
$LiCHI_2$	THF	−110 (slow)	145
$LiCHI_2$	THF	−95	146

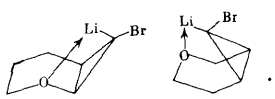
Table 2 shows that halogenolithiomethanes are relatively stable, like halogenolithiobenzenes, only in solutions containing ethers or trialkylamines. According to D'yachenko and Nefedov[147], trichloromethyl-lithium exists, like lithium alkyls and other aliphatic organolithium compounds[124], in the form of the tetrameric complex $(LiCCl_3)_4 \cdot (R_2O)_4$ in an ether–hydrocarbon medium. It follows from the results of two investigations[102,131] that

there is also a possibility of the existence of mixed association complexes of butyl-lithium with monohalogenolithiomethanes. The complex of trichloromethyl-lithium with tetramethylethylenediamine having the composition $LiCCl_3.(CH_3)_2NCH_2CH_2N(CH_3)_2$ has been obtained in a crystalline state[148].

Association and the formation of complexes by halogenolithiomethanes in solution have a significant influence, as for halogenolithiobenzenes, on the stability and reactivity of these compounds. Thus the study of the thermal stability of trichloromethyl-lithium in various solvents showed that this compound decomposes with formation of dichlorocarbene as a consequence of a synchronous reaction, the rate of which is determined by the strength of the Li ← OR_2 coordinate bond[42]:



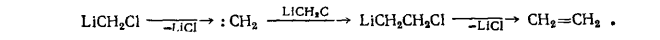
A similar conclusion follows also from the comparison of the stabilities of cyclic and *gem*-bromolithio-compounds, namely *endo*-7-bromo-7-lithionorcarane (X) and its 2-oxa-analogue (XI). According to Seyferth and Lampert[135], compound (X) is unstable in THF above −90°C, while compound (XI), where there is a possibility of the formation of the relatively stable Li ← O intramolecular coordinate bond owing to the proximity of the oxygen and lithium atoms, does not decompose in ether even at −20°C, being one of the most stable of the α-halogeno-derivatives of organolithium compounds. *endo*-7-Bromo-7-lithio-3-oxanorcarane (XII), in certain conformations of which the Li–O distance is shorter by 0.2–0.3 Å than in compound (XI), is still more stable. One should note in this connection that compound (XII) is the only known halogeno-derivative of an organolithium compound which is stable in a hydrocarbon medium[149]:



(XI) (XII)

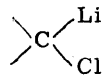
On the other hand, trichloromethyl-lithium obtained by the reaction of CCl_4 with atomic lithium in a solid argon matrix, which is known to be monomeric and not bound in a complex, proved to be unstable even at −230°C,[81] while in THF solutions, for example, it is stable up to approximately −70°C.[41,42]

The association of halogenolithiomethanes has a definite influence also on their reactivity. While the majority of compounds of this type are thermolysed to carbenes and are capable of undergoing their characteristic reactions (the formation of the kinetically independent dichlorocarbene from $LiCCl_3$ was demonstrated by the method of competition kinetics[148,150]), certain halogenolithiomethanes, for example $LiCH_2Cl$ or $LiCHCl_2$, give rise to the formal dimers ($CH_2{=}CH_2$, CHCl=CHCl) on thermal decomposition in solution instead of the kinetically independent carbenes[101,143]. This type of reaction is apparently associated with the rapid insertion of the highly reactive carbene (:CH_2, :CHCl) in the carbon–lithium bond of the initial compound within the cage of the initial association complex, for example, $(LiCH_2Cl)_4(R_2O)_4$:

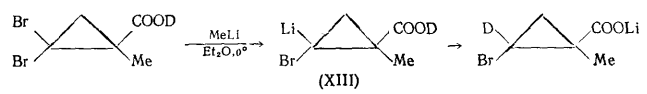


This was confirmed by the observation[147] that even the much less reactive dichlorocarbene formed on decomposition of the mixed association complex $LiCCl_3.(PhLi)_3.(THF)_4$ reacts almost completely with phenyl-lithium (forming $PhCLiCl_2$ and then tolane[127]) without emerging from the cage of the initial association complex.

It follows from the data in Table 2 that the stability of halogenolithiomethanes depends on the nature of the halogen. Evidently, as for halogenolithiobenzenes, there is a tendency for the stability of halogenolithiomethanes and related compounds to decrease with increase of the atomic number of the halogen, but in many instances this type of dependence is masked by other factors and it is extremely difficult to trace it on the basis of the available literature data. According to Talalaeva and Kocheshkov[142], $LiCF_3$ in ethereal solution has T_d = −50–75°C and certain fluorolithiomethanes decompose in the same temperature range[151]. Perfluoroisopropyl-lithium is stable in ether only at −78°C.[152]

Trifluoromethyl-lithium decomposes in THF at −65°C[42]. Similar values of T_d (−65–75°C) are characteristic of αα-dichlorobenzyl-lithium, a series of its substituted derivatives, and many other compounds containing the  group[136,153,154]. However, $LiCHCl_2$ is a much more stable compound (T_d = 30°C in THF) and *exo*-7-chloro-7-lithionorcarane and $LiCH_2Cl$ are more labile (T_d = 110°C). According to Kobrich[7], the lability of chloromethyl-lithium is caused by its high basicity, which ensures its autocatalytic decomposition via an *Elcb* mechanism.

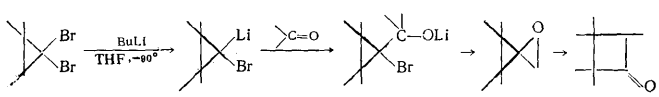
Bromo-derivatives of methyl-lithium, i.e. $LiCHBr_2$ and $LiCBr_3$, have decomposition temperatures T_d close to those of $LiCCl_3$ and the majority of other chloro-derivatives; however, slow decomposition of these compounds is observed at much lower temperatures (approximately −100°C).[144] The acid (XIII), formed when equimolar amounts of methyl-lithium and of the corresponding dibromo-acid react in ether, exhibits some stability even at 0°C. The rate of exchange of bromine for lithium exceeds the rate of the corresponding salt formation reaction to such an extent that the latter is an intramolecular process[155]:



(XIII)

The exact values of T_d for the two known iodolithiomethanes $LiCH_2I$ and $LiCHI_2$[145,146] have not been determined, but it has been shown that these compounds are relatively stable between −90° and −100°C.

Owing to the development of simpler (particularly hydrolytic[156]) methods for the generation of carbenes from halogenomethanes, the decomposition reactions of halogenomethyl derivatives of lithium are nowadays rarely used for the conversion of olefins into cyclopropanes. On the other hand, complex carbenes, mainly different substituted cyclopropylidenes (see above), are still generated almost exclusively by methods of organolithium chemistry. In some cases halogeno-derivatives of organolithium compounds are used at low temperatures also as organolithium reagents, for example[157]:



Many halogenolithiomethanes with different organoelement groups have been synthesised and characterised by the exchange reactions of organolithium compounds with organoelement derivatives (particularly halogen-containing derivatives). However, the majority of these compounds, particularly the trimethylsilyl and trimethylstannyl derivatives of chlorolithio- and bromolithio-methanes, are readily involved in intermolecular reactions of the S_N2 type instead of undergoing the carbene decomposition[158,159]. On the other hand, the decomposition of Ph_3PbCCl_2Li, formed when $(Ph_3Pb)_2CCl_2$ is treated with butyl-lithium, apparently proceeds with the intermediate formation of extremely interesting metallocarbenes[160]:

$$Ph_3PbCCl_2Li \begin{cases} \longrightarrow Ph_3PbCl + Li\ddot{C}Cl, \\ \longrightarrow Ph_3Pb\ddot{C}Cl \rightarrow Ph_3PbCl + :C: . \end{cases}$$

The available data about the halogenomethyl derivatives of other alkali metals are so far limited to the report of the synthesis of several sodium and potassium compounds, which are readily formed when halogenomethanes are treated with the corresponding bistrimethylsilylamides, for example[161]:

$$(Me_3Si)_2NNa + HCBr_3 \rightarrow NaCBr_3 + (Me_3Si)_2NH .$$

In contrast to lithium compounds, the analogous sodium and potassium derivatives proved to be more stable in ether than in THF. Furthermore, contrary to expectation, they are more stable in the majority of cases than the corresponding lithium and even magnesium compounds (Tables 2–4).

Table 3. Thermal stabilities of halogenomethyl derivatives of sodium and potassium in ether[161].

Compound	T_d, °C
NaCClBrH	−30 (slow decomp.)
$NaCHBr_2$	−30 (slow)
$NaCBr_3$	−77 (slow)
$KCHBr_2$	−65 (very fast)
$KCBr_2SiMe_3$	−25 (fast)
$KCBr_3$	←120

Table 4. Thermal stabilities of halogenomethyl derivatives of Grignard reagents.

Compound	T_d, °C		References
	THF	THF + 20% HMP	
CF_3MgCl	decomposes at instant of formation at −115°C	decomposes at instant of formation at −115°C	164
CCl_3MgCl	−65 (very fast)	−65 (very fast)	164
CBr_3MgCl	—	−75 (very fast)	164
$CHBr_2MgCl$	−55	−45	164
$CH_2BrMgCl$	−55 (slow)	—	164
CH_2IMgCl	−55	−45	164
CHI_2MgCl	−85		146

A general method for the synthesis of monobromocyclopropanes has been developed on the basis of the decomposition of $NaCHBr_2$:[162]

$$(Me_3Si)_2NNa + CH_2Br_2 \xrightarrow[-(Me_3Si)_2NH]{} NaCHBr_2 \xrightarrow[-NaBr]{} :CHBr \longrightarrow \text{(Br, H)} \quad (30-50\%) .$$

2. Halogenomethyl Derivatives of Magnesium

Like their lithium analogues, compounds of the type CX_3MgX are obtained by the exchange reaction of the corresponding halogenomethanes with stable Grignard reagents at low temperatures in an ethereal medium[163,164]. Owing to their extremely low basicity, Grignard reagents are not involved in H-metallation reactions and are capable of substituting only halogen atoms in halogenolithiomethanes[164]:

$$CHBr_3 + \text{iso-PrMgCl} \rightarrow CHBr_2MgCl + \text{iso-PrBr},$$
$$CHBr_2Cl + \text{iso-PrMgCl} \rightarrow CHBrMgCl + \text{iso-PrBr} .$$

Like the analogous lithium compounds, halogenomethyl derivatives of organomagnesium compounds are stable only in solution and at extremely low temperatures (Table 4), decomposing on heating with formation of the corresponding carbenes:

$$CX_3MgX \rightarrow :CX_2 + MgX_2 .$$

The decomposition of CCl_3MgBr, formed when CCl_4 is treated with EtMgBr or PhMgBr at relatively high temperatures (20–60°C), proceeds not only via the carbene pathway but also via a free-radical pathway[165]. It follows from the data in Table 4 that halogenomethyl Grignard reagents have thermal stabilities very similar to those of the corresponding lithium compounds. Thus the decomposition temperatures T_d of CCl_3MgCl and CBr_3MgCl correspond to those of $LiCCl_3$ and $LiCBr_3$ (Table 2). On the other hand, $CHBr_2MgCl$ is somewhat more stable than $LiCHBr_2$, while CF_3MgCl is characterised by a much lower stability than $LiCF_3$, being in general one of the least stable halogeno-derivatives of organometallic compounds. An increase of the polarity of the medium [the replacement of THF by 20% solution of hexamethylphosphoramide (HMP)] leads to an increase of the stability of certain halogenomethyl derivatives of cadmium, which is believed[164] to indicate intramolecular halogen–magnesium coordination. However, the stabilisation may also be a consequence of the strengthening of the $Mg \leftarrow OR_2$ coordinate bond, the dissociation of which must precede the carbene decomposition according to some of the present authors' data[41,42].

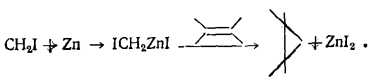
Like the corresponding organolithium compounds, Grignard reagents of the type $R_3MCHXMgX$ (M = Si or Sn; X = halogen) do not tend to undergo the carbene decomposition, forming readily in solution products of reactions of the S_N2 type[159].

3. Organozinc and Organocadmium Compounds

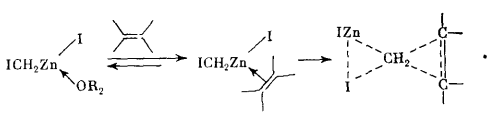
Organozinc compounds are widely used as reagents for the introduction of the methylene group, the so called Simmons–Smith reaction[8,166,167], based on the employment of methylene halides (usually CH_2I_2) and activated zinc powder, being of greatest preparative value. In view of the lower activity of the metal, halogenomethyl derivatives of zinc of the type XCH_2ZnX show a higher thermal stability than the corresponding derivatives of alkali metals and magnesium. It has been shown[104] that ICH_2ZnI, formed by the reaction of methylene iodide with activated zinc in ether, is completely stable in solution at 0–20°C, decomposing slowly with liberation of ethylene at the boiling point of the solvent.

In the presence of olefins, the decomposition of this compound leads to the corresponding cyclopropanes. The Simmons–Smith reaction, usually carried out by refluxing

a mixture of methylene iodide and an olefin with the zinc–copper couple in ether, is at present one of the commonest methods for synthesising cyclopropane hydrocarbons:



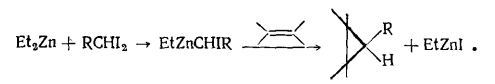
According to Blanchard and Simmons[104], the formation of cyclopropanes by the Simmons–Smith reaction is a stereoselective process in which the olefin is attacked by the electrophile, which corresponds to the possibility of the involvement of singlet methylene or its complex. The composition of the side products of the reaction, among which ethylene and a number of compounds usually formed on reaction of singlet methylene with the solvent have been detected, is also consistent with this hypothesis. On the other hand, the reaction is of second order overall (of first order with respect to the organozinc compound and the olefin), while the intermediate has more stringent steric requirements than the free methylene[104]. Accordingly, it has now been assumed that the Simmons–Smith reaction proceeds without the formation of kinetically independent methylene and the CH_2 fragment is transferred from the organozinc compound to the olefin via a five-centre transition state[6,8,104]. On the other hand, the dependence of the ease of decomposition of ICH_2ZnI on the solvent is analogous to that observed for halogeno-derivatives of organolithium compounds: despite the much higher temperature, this compound is completely stable in boiling THF, but causes the introduction of the methylene group into olefins in ether. In conformity with the above ideas, this implies that the decomposition of the organozinc methylene precursor includes the interaction of the halogen electron pair with the free orbital of the metal, arising when the Zn ← O etherate linkage is ruptured. In this case, the second order of the reaction may be a consequence of the displacement of the ether by the olefin and the subsequent rapid decomposition of the resulting unstable complex:



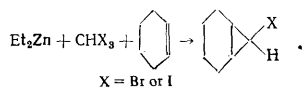
Under mild conditions, methylene halides do not react with ordinary zinc powder and the nature of the initial substances, the yields of the products of the Simmons–Smith reaction, and its duration depend to a large extent on the method used to activate the zinc. The galvanic zinc–copper couple with a low copper content, prepared by treating zinc powder with aqueous solutions of copper salts (sulphate[166–168] or acetate[169]), is usually employed for the reaction. A mixture of zinc powder with copper(I) chloride also exhibits a high activity in the reaction[170].

The zinc–copper couple, prepared using $CuSO_4$, reacts in ether only with CH_2I_2 and CH_2ClI.[167] On the other hand, when zinc is activated by copper acetate, it is possible to involve in the reaction also CH_2Br_2.[169] However, the most effective method of carrying out the Simmons–Smith reaction is associated with the use of the zinc–silver couple followed by the removal of the salts formed during the reaction as the pyridine complexes[171]. This mode of reaction makes it possible to introduce the methylene group (with a high yield of cyclopropanes) not only into olefins but also into many compounds with functional groups, for example unsaturated ketones, ethers, enol ethers, and enamines.

The conversion of olefins into cyclopropanes as a result of the joint treatment with diethylzinc and *gem*-di-iodoalkanes proceeds via a similar pathway—with the intermediate formation and decomposition of halogenomethyl derivatives of zinc[172]:

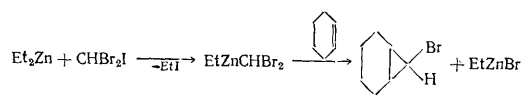


When this reaction is carried out with dihalogenoiodomethanes of the type CHIXY (X, Y = F, Cl, or Br), the corresponding monohalogenocyclopropanes are formed in yields up to 90%;[173] monoiodo- and monobromo-cyclopropanes are obtained in high yields by this reaction from CHI_3[174] and $CHBr_3$:[175]

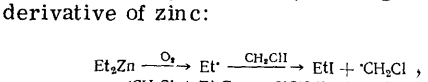


In the presence of benzene and its alkali derivatives, the corresponding cycloheptatrienes are obtained from $CHBr_3$ and Et_2Zn.[175] An attempt to involve chloroform in a reaction of this type has been described: 7,7-dichloronorcarane was synthesised in a low yield when cyclohexene was treated jointly with $CHCl_3$ and diphenylzinc[176].

When trihalogenomethanes containing different halogen atoms in the same molecule were used in the reaction with diethylzinc, the nature of the product was determined by the mobility of the halogen in the exchange reaction[120,121]. Thus 7-bromonorcarane can be obtained from $CHBr_2I$, diethylzinc, and cyclohexene, ethyl iodide being formed exclusively in the first stage of the reaction[172]:

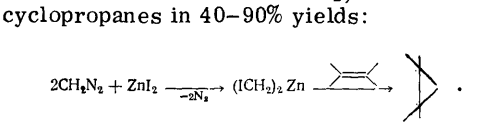


The interaction of organozinc compounds with methylene halides or haloforms is catalysed by oxygen[177]. Thus the reaction of Et_2Zn with CH_2ClI in nitrogen leads to norcarane in 61% yield after 6 h in the presence of cyclohexene; when dry air is passed through the reaction mixture, the same reaction proceeds to the extent of 99% in 30 min. This result undoubtedly indicates the involvement of free radicals in the exchange reaction, leading to a halogenomethyl derivative of zinc:



The involvement of free radicals in this reaction has also been demonstrated by the observation of the considerable polymerisation of styrene when an attempt was made to introduce the bromomethylene group into the latter by treatment with diethylzinc and bromoform in air[175].

Like the halogenomethyl derivatives of zinc described above, symmetrical compounds of the type $Zn(CHRX)_2$, which can be readily obtained by the thermolysis of the corresponding diazoalkanes in the presence of zinc salts, are also active agents for the introduction of the methylene group[178–180]. Thus, bis(iodomethylzinc), formed by the reaction of diazomethane with ZnI_2, reacts with olefins to form cyclopropanes in 40–90% yields:



$ZnCl_2$ reacts similarly with diazomethanes, forming the tetrameric etherate $[Zn(CH_2Cl)_2(OEt_2)_2]_4$,[179] the interaction of which with cyclohexene in ether gives rise to norcarane. The decomposition of bis(chloromethyl)zinc is appreciably catalysed by the addition of $ZnCl_2$ and proceeds at an appreciable rate in the presence of this salt even at 0°C, which indicates a weakening of the coordinate bond in the etherate of the $ClZnCH_2Cl$ formed.

An effective agent for the introduction of the methylene group is obtained on decomposition of diazomethane in the presence of zinc benzoate and ZnI_2:[181]

$$(PhCOO)_2Zn \xrightarrow{CH_2N_2} (PhCOOCH_2)_2Zn \xrightarrow{ZnI_2} \rightarrow PhCOOCH_2ZnI \longrightarrow \text{(yield 66\%)} .$$

Aryl- and diaryl-diazomethanes[182-184] are also readily decomposed by zinc salts, forming the corresponding arylhalogenomethyl derivatives of organozinc compounds, the decomposition of which in the presence of olefins leads to cyclopropanes. The stability of the zinc compounds formed in this reaction decreases as a function of the nature of the halogen in the sequence Cl > Br > I.[183]

Bis(dichloromethyl)zinc was obtained by treating $ZnCl_2$ with dichloromethyl-lithium[143]:

$$2LiCHCl_2 + ZnCl_2 \rightarrow (Cl_2CH)_2Zn + 2LiCl .$$

Like ICH_2ZnI, this compound is completely stable in boiling THF, but is converted into 7-chloronorcarane in a low yield on prolonged refluxing with cyclohexene in benzene.

Diethylcadmium reacts with *gem*-di-iodoalkanes similarly to diethylzinc, forming the corresponding cyclopropanes in the presence of olefins[185]:

$$Et_2Cd + RCHI_2 \longrightarrow \text{(R=H, Me, Ph)} .$$

The yields of the reaction products for zinc and cadmium compounds with analogous structures are similar.

Virtually identical mixtures, containing 30–40% of 1-chloropropane, were obtained also in the reactions of diethylzinc and diethylcadmium with $CHCl_3$ and CCl_4.[186] The formation of 1-chloropropene apparently indicates the intermediate generation and subsequent carbene decomposition of compounds of the type $RMCCl_2Et$:

$$RMCCl_2Et \xrightarrow{-RMCl} :CClEt \rightarrow ClCH{=}CHMe ;$$
$$R = Et, \text{ or } Cl;\ M{=}Zn,\ Cd .$$

Virtually exclusive formation of propene, which is apparently also a consequence of the carbene–olefin isomerisation, has been observed in the reaction of 1,1-di-iodopropane with the zinc–copper couple in the presence of cyclohexene[168].

Like zinc salts, CdI_2 reacts with diazomethane to form $ICdCH_2I$, which, however, is a much less active agent for the introduction of the methylene group than $IZnCH_2I$.[179]

4. Organomercury Compounds

The halogenocarbenes, formed when trihalogenomethyl compounds react with bases or on thermolysis of salts of trihalogenoacetic acids, are readily inserted into the Hg–X bonds of compounds of the type RHgX (R = aryl, alkyl, or halogen; X = halogen), giving rise to the corresponding $RHgCX_3$, for example:

$$PhHgCl + CHCl_3 + t\text{-}BuOK \rightarrow PhHgCCl_3 + t\text{-}BuOH + KCl ,$$
$$PhHgBr + Cl_3COONa \rightarrow PhHgCCl_2Br + CO_2 + NaCl .$$

These compounds decompose at moderate rates in the temperature range which is extremely convenient for carrying out chemical reactions (20–80°C) with formation of RHgX and the corresponding carbene:

$$PhHgCCl_3 \rightarrow PhHgCl + :CCl_2 .$$

The decomposition of such compounds, carried out in solvents (dimethoxyethane, benzene, THF, CH_2Cl_2, etc.) which are inert with respect to the carbenes generated, leads to the corresponding cyclopropane compounds in the presence of unsaturated compounds. Owing to the neutral medium and the absence of other reactive intermediates (for example CX_3^- anions), the reaction proceeds exceptionally smoothly, giving high yields of cyclopropanes, not only with olefins but also with many of their derivatives having functional groups, being complicated only by the formation of $CX_2{=}CX_2$ dimers owing to the occurrence of reactions of the type

$$RHgCX_3 + :CX_2 \rightarrow RHgCX_2CX_3 \rightarrow RHgX + CX_2{=}CX_2$$

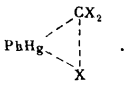
to a slight extent. Furthermore, since the carbene decomposition of trihalogenomethyl derivatives of mercury is reversible and the RHgX compounds formed on decomposition can be readily used virtually without loss for the regeneration of the initial reagent, compounds of this type are regarded nowadays as the most convenient agents for the transfer of carbenes to unsaturated compounds.

The study of the kinetics of the thermolysis of $PhHgCl_2Br$,[187] leading to PhHgBr and the corresponding *gem*-dichlorocyclopropanes with almost quantitative yields in the presence of olefins, showed that in the initial stage the reaction is of first order with respect to the organomercury compound and of zero order with respect to the olefin. On the other hand, the rate of reaction diminishes following the addition of PhHgBr and depends to some extent on the nature of the olefin, which can be readily interpreted by postulating a sequence of two stages, the slow stage involving the reversible formation of free dichlorocarbene:

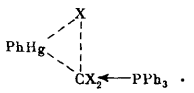
$$PhHgCCl_2Br \overset{slow}{\rightleftharpoons} PhHgBr + :CCl_2$$
$$:CCl_2 + \text{olefin} \xrightarrow{fast} \text{dichlorocyclopropane} .$$

The involvement in this reaction of the kinetically independent carbene was also confirmed by the virtual identity of the relative rates of introduction of the dichloromethylene group into various olefins (determined by the method of competition kinetics) in the generation of dichlorocarbene by the thermolysis of $PhHgCCl_3$, $LiCCl_3$, and CCl_3COONa, by treating $CHCl_3$ with t-BuOK,[150] and by the high-temperature pyrolysis of chloroform[148]. The intermediate formation of singlet $:Cl_2$ is also indicated by the explicit electrophilic mechanism of the conversion of olefins into dichlorocyclopropanes by treatment with $PhHgCCl_2Br$ [188] and $PhHgCCl_3$.[148,150,188] Since the rate of decomposition of compounds of the type $RC_6H_4HgCCl_2Br$ depends to only a slight extent on the nature of R (R = H, *p*-F, *p*-Cl, *p*-MeO, or *p*-Me), it is suggested that this reaction proceeds similarly to the decomposition of other organometallic compounds discussed above, in a single stage via a transition state produced as a result of the

coordination of the halogen electron pair to the free metal orbital[189]:



Since the bulky central mercury atom in the compounds $RHgCX_3$ is incapable of forming sufficiently stable complexes with weak Lewis bases, the rate of decomposition of these compounds is to a large extent independent of the nature of the solvent (benzene, dimethoxyethane, THF). Furthermore, in contrast to the analogous compounds of complex-forming metals, the decomposition of the mercury compounds is accelerated in the presence of strong Lewis bases (amines and phosphines), apparently owing to the formation of the complex involving the free orbital of the carbene[187]:



On the other hand, as for the α-halogenomethyl derivatives of other metals, the stability of the mercury compounds under consideration is determined by the nature of the halogen: in conformity with the strength of the C–X bond and the radius of the X atom, the rate of decomposition of $PhHgCX_3$ increases in the sequence $F \ll Cl < Br < I$. The same relation determines also the mode of decomposition of mixed trihalogenomethyl compounds of the type $PhHgCXY_2$ and PhHgCXYZ (Table 5).

Table 5. Thermal stabilities of trihalogenomethyl derivatives of phenylmercury[9].

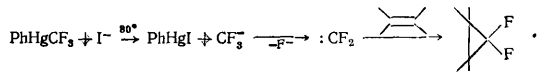
Compound	Carbene	Total decomposition time in benzene	
		at 80°C	at 20°C
$PhHgCCl_2I$	CCl_2	instantaneous	24 h
PhHgCClBrI	CClBr	3 min	4 days
$PhHgCBr_3$	CBr_2	–	15–16 days
$PhHgCClBr_2$	CClBr	–	15–16 days
$PhHgCFBr_2$	CFBr	20 min	3 days
$PhHgCCl_2Br$	CCl_2	2 h	11 days
$PhHgCCl_3$	CCl_2	48 h	—
$PhHgCCl_2F$	CClF	48 h	—

According to the mechanism adopted for the decomposition reaction, a decrease in the electronegativity of the group R in $RHgCX_3$ should lead to the destabilisation of the molecule. Indeed alkyl and cycloalkyl derivatives of trihalogenomethylmercury are less stable than the corresponding aromatic compounds[190,191]. In particular, cyclo-$C_6H_{11}HgCX_3$, formed when the corresponding cyclo-$C_6H_{11}HgX$ reacts with CHX_3 (X = Cl or Br) and t-BuOK in THF at −60°C,[191] are so reactive that they are much less readily available than iodo-derivatives of the type $PhHgCX_2I$.

In contrast to the corresponding iodo-, bromo- and chloro-derivatives, trifluoromethylphenylmercury and other trifluoromethyl derivatives of mercury, which are readily obtained by the pyrolysis of the corresponding trifluoroacetates[102],

$$Hg(OCOCF_3)_2 \xrightarrow{300^\circ} CF_3HgOCOCF_3$$

do not decompose with formation of $:CF_2$ even at relatively high temperatures. Thus $PhHgCF_3$ does not change on heating in solution for eleven days up to 140°C.[9,192] On the other hand, like other $RHgCX_3$ derivatives, these compounds readily form carbenes in the presence of NaI;[192–194] however, in this case the reaction proceeds with the intermediate formation of the CX_3^- anions:



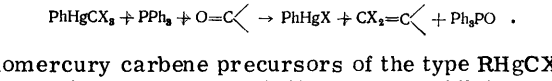
The formation of carbanions under these conditions was demonstrated by the formation of the corresponding trihalogenomethyldimethylmethanols on decomposition of $PhHgCCl_3$ and $PhHgCCl_2Br$ in the presence of NaI in acetone[195]. In contrast to $PhHgCF_3$, the compounds $ClHgCF_3$ and $BrHgCF_3$ do not decompose in the presence of NaI owing to the formation of stable complexes of the type $NaClHgCF_3$ and $Na_2ClI_2HgCF_3$.[104]

Table 6. Carbenes obtained from halogenomethyl derivatives of mercury.

Organomercury compound	Carbene formed	Refs.	Organomercury compound	Carbene formed	Refs.
1	2	3	1	2	3
$Hg(CH_2Br)_2$	CH_2	196	cyclo-$C_6H_{11}HgCClBr_2$	CClBr	191
$Hg(CH_2I)_2$	CH_2	197	$PhHgCCl_2F$	CClF	206
$IHgCH_2I$	CH_2	197	$PhHgCBr_2F$	CBrF	207
$PhCH_2HgCH_2I$	CH_2	198	$PhHgCCl_2CF_3$	$CClCF_3$	208
$PhHgCHCl_2$	CHCl	199	$PhHgCClBrCF_3$	$CClCF_3$	208
PhHgCHClBr	CHCl	200	$PhHgCCl_2Ph$	CClPh	209
$PhHgCHBr_2$	CHBr	200			
$PhHgCHClCO_2Et$	$CHCO_2Et$	201	$PhHgCCl_2CON$	CClCON	210
$Hg(CCl_3)_2$	CCl_2	201			
$ClHgCCl_3$	CCl_2	202			
$PhHgCCl_3$	CCl_2	188	$PhHgCBr_2CON$	CBrCON	211
$PhHgCCl_2Br$	CCl_2	188			
$PhHgCCl_2I$	CCl_2	203	$PhHgCCl_2SO_2Ph$	$CClSO_2Ph$	201
n-$PrHgCCl_3$	CCl_2	190	$PhHgCBr_2SO_2Ph$	$CBrSO_2Ph$	201
n-$PrHgCCl_2Br$	CCl_2	190	$PhCH_2CH_2HgCCl_2CO_2Me$	$CClCO_2Me$	201
cyclo-$C_6H_{11}HgCCl_3$	CCl_2	191	$PhHgCCl_2CO_2Me$	$CClCO_2Me$	201
cyclo-$C_6H_{11}HgCCl_2Br$	CCl_2	191	$PhHgCClICO_2Me$	$CClCO_2Me$	201
$Hg(CBr_3)_2$	CBr_2	204	$PhHgCClBrCO_2Me$	$CClCO_2Me$	212
$PhHgCBr_3$	CBr_2	188	$PhHgCBr_2CO_2Me$	$CBrCO_2Me$	212
cyclo-$C_6H_{11}HgCBr_3$	CBr_2	191	$PhHgCClFCO_2R^*$	$CFCO_2R^*$	213
$PhHgCClBr_2$	CClBr	188	$PhHgCBrFCO_2R^*$	$CFCO_2R^*$	213
PhHgCClBrI	CClBr	205	$Hg(CCl_2SiMe_3)_2$	$CClSiMe_3$	214

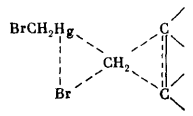
* R=Me, Et

The method of the liquid-phase thermolysis of halogenomethyl derivatives of mercury is widely used nowadays to synthesise various cyclopropane derivatives, many of which are formed in quantitative or nearly quantitative yields (Table 6), including the reaction involving weakly nucleophilic olefins. Among the applications of the carbene decomposition of organomercury compounds, mention should be made of the synthesis of numerous organic derivatives of other elements[9] and also the single-stage version of the Wittig reaction[215]:

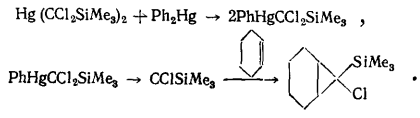


Organomercury carbene precursors of the type $RHgCX_3$, containing electronegative substituents R, exhibit a reduced reactivity and in some cases do not form free carbenes on liquid-phase thermolysis. Thus $Hg(CH_2Br)$ withstands prolonged boiling in benzene without appreciable decomposition, but readily introduces the methylene group

into olefins under the same conditions, evidently via the formation of an intermediate complex of the type[216]

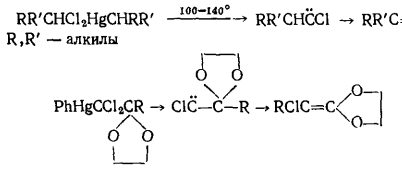


$BrHgCH_2Br$, which can introduce the methylene group into olefins only with low yields and under more severe conditions, is still more stable. However, it has been shown[196] that thermolysis of this and certain other stable halogenomethyl derivatives of mercury is greatly accelerated in the presence of Ph_2Hg owing to a redistribution reaction with formation of the corresponding substituted derivatives of phenylmercury. Thus $Hg(CCl_2SiMe_3)_2$ reacts with cyclohexene at 120°C to form 7-chloro-7-trimethylsilylnorcarane in 24% yield, while in the presence of Ph_2Hg the yield is 62%:[214]



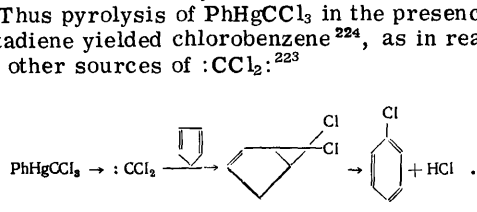
$:CBrSiMe$[217] and $:CHSiMe_3$[217,218] can be generated similarly from the corresponding symmetrical compounds.

More complex carbenes can also be generated from α-halogeno-derivatives of organomercury compounds by the method of liquid-phase thermolysis, but these species usually isomerise to the corresponding unsaturated compounds, for example[219-221]:



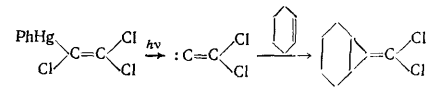
Instead of the carbene decomposition, 1,1-dichloroethylphenylmercury undergoes thermal dehydrochlorination with formation of chlorovinylmercury[222].

Trihalogenomethyl derivatives of mercury generate dihalogenocarbenes not only in the liquid but also in the gas phase. Thus pyrolysis of $PhHgCCl_3$ in the presence of cyclopentadiene yielded chlorobenzene[224], as in reactions involving other sources of $:CCl_2$:[223]



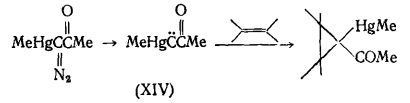
The intermediate formation of dihalogenocarbenes in the gas-phase pyrolysis (at 250–550°C) of $PhHgCClBr_2$, $PhHgCCl_2Br$, $PhHgCCl_3$, $Hg(CCl_3)_2$, and $ClHgCCl_3$ was demonstrated by their low-temperature stabilisation in an argon matrix with subsequent investigation using infrared spectroscopy[82,224-228]. The valence angle of this carbene (106° ± 4°) was found from the isotopic splitting of the $:CCl_2$ stretching vibration bands and the singlet state of this species was thereby demonstrated[82].

In contrast to the liquid-phase reactions, the gas-phase pyrolysis of trihalogenomethyl derivatives of mercury leads to the corresponding dihalogenomethyl radicals as well as carbene. The rate of formation of the radicals depends on the nature of the initial compound and generally increases with temperature[228], owing to the high degree of excitation of the vibrational-rotational levels of the molecule, which hinders the formation of the halogen–mercury bond in the transition state of the carbene decomposition reaction. Nevertheless the carbene pathway in the pyrolytic decomposition of these compounds predominates up to very high temperatures (about 500°C). In conformity with these ideas, the more vigorous excitation of molecules attainable following the ultraviolet irradiation of $PhHgCCl_3$ and $Hg(CCl_3)_2$ proceeds with the exclusive formation of trihalogenomethyl radicals[229,230]. On the other hand, in certain cases ultraviolet photolysis of α-halogeno-derivatives of organomercury compounds leads also to the formation of carbenes, for example[231]:



The above examples of the generation of carbenes from organomercury compounds are based on the use of α-halogeno-derivatives, a characteristic reaction pathway for which is α-decomposition. However, there are also examples in the literature of carbene-type photochemical decomposition of other organomercury compounds, particularly α-mercuri-derivatives of diazo-compounds.

Ultraviolet photolysis (λ > 335 nm) of methylmercuridiazoacetone ($MeHgCN_2OMe$) proceeds analogously to the photolysis of other diazo-compounds, leading to the metal-containing carbene $MeHgC\ddot{C}OMe$ (XIV), which interacts with olefins to form the corresponding cyclopropane derivatives in yields of 70–90%:[232]



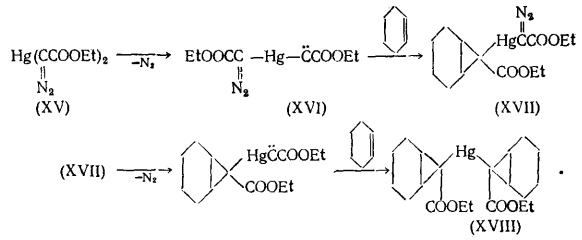
(XIV)

Like the other carbenes formed in the photolysis of diazo-compounds, compound (XIV) is probably generated in the triplet state, which rapidly relaxes to the singlet state (by virtue of the presence of the heavy metal atom next to the carbene centre), which can be inferred from the stereospecificity of the reaction with olefins and the absence from the reaction mixture of products of the Wolf rearrangement, which is characteristic of triplet ketocarbenes[233].

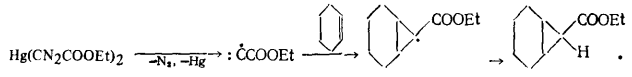
Analogous photochemical decomposition at λ > 335 nm, with formation of mercury-containing singlet carbenes, is also characteristic of many other compounds of the type $RHgC(N_2)X$ (where R = Me, Et, iso-Pr, t-Bu, Ph, or $PhCH_2$ and X = Me, Ph, CN, COMe, or COOMe), which are readily formed when RHgOEt reacts with diazo-compounds $XHCN_2$.[234] When the energy of the irradiation (λ < 280 nm) of a compound of this type increases, the mercury-containing fragment is split off together with a nitrogen molecule, forming intermediate compounds of formally univalent carbon—carbene-radicals or carbynes $:C\dot{X}$.

Similar relations are also observed in the ultraviolet photolysis of bis(diazoethoxycarbonylmethyl)mercury [$Hg(CN_2COOEt)_2$] (XV).[235-237] Thus compound (XV) initially splits off one nitrogen molecule on long-wavelength irradiation (λ > 335 nm) with formation of the singlet mercury-containing carbene (XVI), which reacts with cyclohexene to form the corresponding norcarane (XVII),

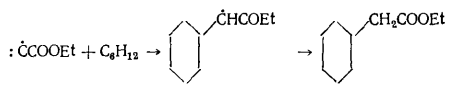
the subsequent decomposition of which, followed by the reaction with cyclohexene, leads to compound (**XVIII**):



The reaction involving the insertion of compound (**XVI**) in the allylic C–H bond of cyclohexene takes place simultaneously. More severe irradiation ($\lambda < 280$ nm) results in extensive decomposition of (**XV**), giving rise to the formation of ethoxycarbonylcarbyne (:CCOOEt) (in the doublet $^2\Pi$ ground state), which undergoes stereoselective addition to the C=C bonds of olefins like singlet carbenes. The ethoxycarbonylcyclopropyl radicals formed as a result of this reaction, subsequently deprotonate the initial olefin molecule, being converted into the corresponding ethoxycarbonylcyclopropane, for example:



The same intermediate species is probably formed also in the thermolysis of $Hg(CN_2COOEt)_2$.[235] Photolysis of this compound in cyclohexane leads to products of the insertion of ĊCOOEt in the C–H bond:



5. Halogenomethyl Derivatives of Group III Elements

The halogenomethyl derivatives of Group III elements have been inadequately investigated as potential sources of carbenes, although the available literature data definitely indicate the validity also for this series of compounds of the fundamental relations determining the reactivity of organometallic carbene precursors.

Thus trifluoromethyldifluoroborane reacts with amines to form the extremely stable complexes $CF_3BF_2.NR_3$, but decomposes in a free state with formation of polymeric difluoromethylene[238]:

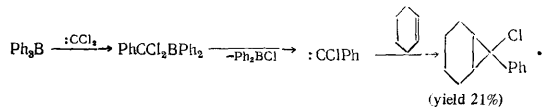
$$CF_3BF_2 \xrightarrow{-BF_3} :CF_2 \rightarrow (CF_2)_n \ .$$

In contrast to the α-decomposition reactions of halogenoderivatives of organometallic compounds discussed above, the latter reaction is catalytic and proceeds vigorously in the presence of traces of oxygen, moisture, and certain organic compounds. In the absence of these promoting agents, CF_3BF_2 is stable at room temperature[238]. CF_3BBu_2 exhibits a similar reactivity[238].

Compounds of the type $(RCH_2CH_2)_2BCCl_2CH_2CH_2R$ (R = Me or Et), formed in the thermolysis of $PhHgCCl_2Br$ in the presence of the corresponding trialkylboranes (80°C, benzene), are unstable under the conditions of their formation and decompose as a result of a series of transformations with elimination of the carbene $(RCH_2CH_2)_2C$:, which isomerises to an olefin. The reaction proceeds with a high degree of conversion and can serve as a preparative method for the synthesis of olefins with an inner double bond[239]:

$$(RCH_2CH_2)_3B \xrightarrow{:CCl_2} (RCH_2CH_2)_2BCCl_2CH_2CH_2R \rightarrow$$
$$\rightarrow RCH_2CH_2BClCCl(CH_2CH_2R)_2 \xrightarrow[-RCH_2CH_2BCl_2]{} :C(CH_2CH_2R)_2 \rightarrow RCH_2CH{=}CHCH_2CH_2R \ .$$

The analogous reaction with triphenylborane leads to $\alpha\alpha$-dichlorobenzyldiphenylborane, which decomposes slowly at 80°C with formation of chlorophenylcarbene:



Chlorophenylnorcarane is formed from $PhB(OMe)_2$ in a somewhat higher yield by an analogous reaction[239].

The method of synthesis of halogenophenyl derivatives of organoelement compounds by the decomposition of diazomethane in the presence of the corresponding halide salts, which was discussed above, is inapplicable to boron compounds, because they give rise to polymethylene exclusively. However, the analogous reaction with $AlCl_3$ in ether yields, together with polymethylene, a mixture of the etherates of chloromethyl derivatives of aluminium of the type $Al(CH_2Cl)_nCl_{3-n}OEt_2$ ($n = 0$–3) and the reaction of CH_2N_2 with R_2AlX (R = alkyl; X = Cl, Br, or I) under the same conditions gives high yields of etherates of the type $R_2AlCH_2X.OEt_2$. These etherates are fairly stable and do not decompose up to 100°C. On the other hand, the free R_2AlCH_2X formed when this reaction is carried out in a hydrocarbon medium are extremely labile and decompose at a high rate even at −10°C:

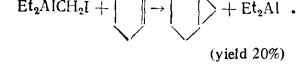
$$R_2AlCH_2X \xrightarrow{-R_2AlX} :CH_2 + CH_2{=}CH_2 \ .$$

The free $RAl(CH_2X)_2$ species formed in the decomposition of CH_2N_2 in the presence of $RAlX_2$ [240,241] exhibit a similar reactivity.

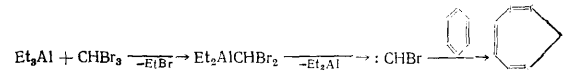
A characteristic feature distinguishing α-halogenomethyl derivatives of aluminium from similar compounds of other metals is the ease with which they add to the multiple bonds of olefins and acetylenes: R_2AlCH_2X forms the corresponding γ-halogenopropyl compounds even at −50°C in the presence of unsaturated hydrocarbons; these products then decompose with formation of cyclopropane derivatives.

Like the "diethylzinc (or diethylcadmium) + CH_2I_2" systems[185], the "triethylaluminium + CH_2I_2" system introduces the methylene group into olefins, probably via the intermediate formation of Et_2AlCH_2I:[242]

$$Et_3Al + CH_2I_2 \rightarrow Et_2AlCH_2I + EtI \ ,$$

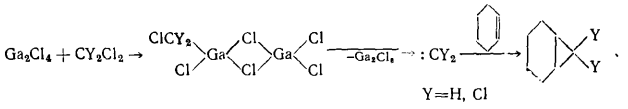


The ability of halogenomethyl derivatives of aluminium to decompose with formation of carbenes is indicated by the analogous reaction of Et_3Al with bromoform in benzene, which leads to bromocycloheptatriene:



The reactions of R_3Al (R = Et or iso-Bu) with CHI_3, $CHCl_3$, CBr_4,[242] and CCl_4 [242,243] also proceeds with the intermediate formation of carbenes.

Carbene decomposition is known to occur also for the analogous compounds of heavier Group III elements. Thus the formation of norcarane and 7,7-dichloronorcarane was observed in the interaction of Ga_2Cl_4 with CH_2Cl_2 and CCl_4 in the presence of cyclohexene[244]:



Y=H, Cl

Like the boron and aluminium compounds, triethylthallium reacts with dichlorocarbene to form $\alpha\alpha$-dichloropropyldiethylgallium, which is unstable and decomposes via the carbene mechanism[190,245,246]:

$$Et_3Tl + PrHgCCl_2Br \xrightarrow[-PrHgBr]{} Et_2TlCCl_2Et \xrightarrow[-EtTlCl]{} :CClEt \rightarrow ClCH{=}CHCH_3 .$$

The reaction of Et_3Tl with CCl_4 or $CHCl_3$ (the latter reaction takes place on heating) gives rise to Et_2TlCCl_3—an unstable compound which decomposes with formation of dichlorocarbene[190,245,246]. The same intermediates are readily formed when $CHCl_3$ interacts with $Et_2TlOCMe$ or Et_2TlNMe_2 at 0°C. The analogous reaction with CH_2Cl_2 leads to the unstable $Et_2TlCHCl_2$, which decomposes, probably with formation of CHCl. The indium compounds $Et_2InOCMe_3$ and Et_2InNMe_2 react with chloroform under much more severe conditions (100–150°C) also forming trichloromethyl compounds which decompose with formation of dichlorocarbene under the reaction conditions[246].

6. Compounds of Group IV Elements

It follows from the above data that the majority of α-halogenomethyl derivatives of Group I–III metals are thermolabile compounds, which decompose via the coordination of the free electron pair of the halogen to a vacant *p* orbital of the metal (n–p coordination). Since the elements of Group IV and subsequent Groups do not have vacant *p* orbitals in the ground state, the single-stage α-decomposition of the halogenomethyl derivatives of these elements can take place only via the coordination of *p* electrons of the halogen to higher sublevels of the metal, which entails an appreciable increase of the activation barrier. On the other hand, the single-stage carbene decomposition of compounds of the elements in the First Period is possible only via the coordination of the *n*-electron pair to the *d* orbital of the next electronic level, which conflicts with the principle of the non-intersection of potential surfaces. As a consequence of this, the thermolysis of such compounds occurs only under very severe conditions, and proceeds exclusively via the homolytic dissociation mechanism, for example[223,249]:

$$Cl_3C{-}CCl_3 \rightleftharpoons 2Cl_3C^{\bullet}$$
$$Cl_3C{-}CCl_3 \rightarrow CCl_4 + :CCl_2$$
$$CCl_2{=}CCl_2 \rightleftharpoons 2\,Cl_2C:$$
$$CCl_2{=}CCl_2 \rightarrow {}^{\bullet}CCl_3 + :CCl .$$

The α-decomposition of compounds of the elements in the higher Fourth–Sixth Periods involves n–d coordination, as a result of which α-halogenomethyl derivatives of these elements are quite stable under the usual conditions, and decompose via the carbene mechanism only at relatively high temperatures (100–400°C). Thus the trichloromethyl derivatives of silicon [Cl_3CSiCl_3,[247,248] CCl_3SiCl_2OEt, $CCl_3SiCl(OEt)_2$, $CCl_3Si(OEt)_3$, $CCl_3SiMeCl_2$, $CCl_3SiCl_2CCl_3$, and CCl_3SiF_3 [248]] form the corresponding *gem*-dichlorocyclopropanes in yields of 30–80% on heating with olefins (100–250°C). A study of the kinetics of the reaction[248] showed that it is of first order and that its rate is independent of the nature of the olefin. Hence it follows that the initial reaction product is free dichlorocarbene:

$$CCl_3SiX_3 \rightarrow :CCl_2 + SiClX_3 ,$$
X=Cl, F, OEt, Me, CCl_3 .

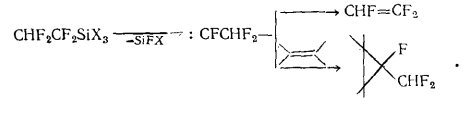
Furthermore, dichlorocarbene and $SiCl_4$ have been detected directly by infrared spectroscopy in an argon matrix as the primary products of the pyrolysis of CCl_3SiCl_3 (together with small amounts of the corresponding free radicals).[249]

In contrast to compounds of other elements, the fluoromethyl derivatives of silicon decompose at much lower temperatures than their chloro-analogues. Thus CF_3SiF_3 smoothly splits off $:CF_2$ even at 100°C:[250]

$$CF_3SiF_2 \xrightarrow[-SiF_4]{} :CF_2 \rightarrow CF_2{=}CF_2 .$$

The cause of the reduced stability of fluoromethyl derivatives of silicon is undoubtedly associated with the considerable energy gain due to the unique stability of the Si–F bond formed (energy 170 kcal $mole^{-1}$ [251]). Possibly H_3SiCH_2F is unstable for the same reason even at 20°C, although other compounds of the type H_3SiCH_2X (X = Cl, Br, or I) are fully stable[252].

In conformity with the greater thermal stability of β-fluoroalkylsilanes, decomposing with formation of olefins only in the range 150–300°C,[253,254] compounds of the type $CHF_2CF_2SiX_3$ (X = F or Me) undergo mainly α-decomposition on thermolysis, forming fluoro(difluoromethyl)carbene. In contrast to alkylcarbenes, the latter converts olefins into cyclopropane derivatives in quantitative yields and isomerises to $CHF{=}CF_2$ only in the absence of unsaturated acceptors[254]:



The difficulty of the carbene–olefin isomerisation was also noted for perfluorovinylidene, generated from an organomercury precursor[255].

When the alkyl chain of substituted silanes contains simultaneously F and Cl atoms, the thermolysis proceeds only with migration of the fluorine atom[247]:

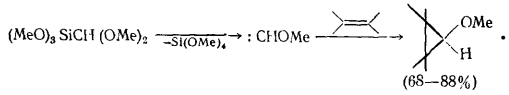
$$CFCl_2CF_2SiCl_3 \xrightarrow{185^\circ} \begin{cases} \xrightarrow[-SiCl_3F]{\alpha\text{-elimination}} CFCl_2FC: \rightarrow CFCl{=}CFCl\ (80\%) , \\ \xrightarrow[-SiCl_3F]{\beta\text{-elimination}} CCl_2{=}CF_2\ (7\%) . \end{cases}$$

Certain compounds of this type have been found to undergo an exchange of Cl and F atoms prior to decomposition[256]. Such an exchange reaction, which is thermodynamically an extremely favourable process, occurs with $CH_3CF_2SiCl_3$ even at 100°C and is in no way complicated by the α-decomposition[256]:

$$CH_3CF_2SiCl_3 \xrightarrow{100^\circ} CH_3CCl_2SiF_2Cl \xrightarrow[-SiF_2Cl_2]{225^\circ} :CClCH_3 \rightarrow CH_2{=}CHCl .$$

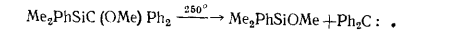
The acetals of silyl-substituted ketones[257] and aldehydes[258] apparently also have low thermal stabilities owing to thermodynamic causes[258]. Thus $(MeO)_3SiCH(OMe)_2$, readily obtained by the reaction of $Cl_3SiSiCl_3$ with $HC(OMe)_3$, decomposes under extremely mild conditions (125°C) with formation of an interesting carbene (methoxymethylene),

which converts olefins into the corresponding methoxycyclopropanes stereospecifically and with high yields[258]:

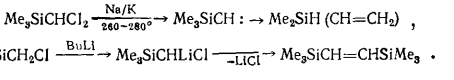


Kinetic data (overall first-order reaction) confirm the formation of free :CHOMe under these conditions.

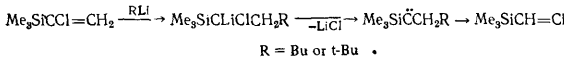
Monomethoxymethylsilanes have a higher thermal stability than the dimethoxy-derivatives but they too are capable of decomposing via the carbene mechanism[257]:



Certain organosilicon carbenes, whose reactivity and particularly their capacity for isomerisation are to a large extent determined by the lability of the C=Si bond, have been obtained from substituted silanes by the methods usually employed for the generation of carbenes. Thus, depending on the method and temperature of its generation, trimethylsilylcarbene isomerises to dimethylvinylsilane[259] or dimerises to 1,2-bis(trimethylsilyl)ethylene[260]:

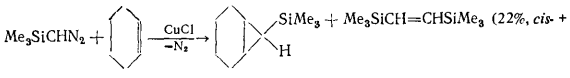


β-Alkylation of α-chlorovinyldimethylsilane probably also proceeds with the intermediate formation of a carbene[261]:

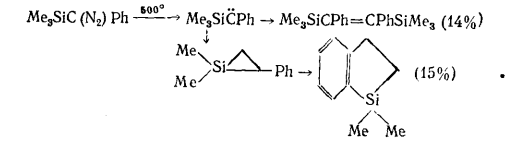


R = Bu or t-Bu .

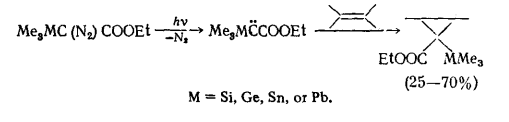
The thermocatalytic decomposition of trimethylsilyldiazomethane under the influence of CuCl in the presence of cyclohexene gives a high yield of trimethylsilylnorcarane, the dimers of the corresponding carbene being formed simultaneously[262]:



The thermolysis of phenyltrimethylsilyldiazomethane also leads to a carbene dimer together with 1,1-dimethyl-1-silaindan—the product of the isomerisation of the carbene, which probably proceeds via the corresponding silacyclopropane[263]:

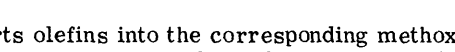


Photolysis of trimethylsilyldiazoacetate and of the analogous germanium, tin, and lead compounds leads, as in the case of the similar organomercury compounds, to substituted ethoxycarbonylcarbenes capable of introducing methylene groups into olefins with high yields[264,265]:



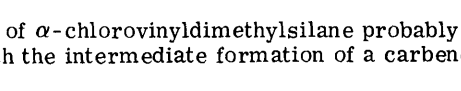
M = Si, Ge, Sn, or Pb.

Siloxycarbenes have been suggested as intermediates in the photolysis of acylsilanes[266]:



When this reaction is carried out in the presence of carbonyl compounds, the corresponding oxirans are formed, i.e. siloxycarbenes exhibit nucleophilic properties[267].

Owing to the considerable coordination unsaturation of the central atom, α-halogenomethyl derivatives of heavy Group IV elements undergo carbene decomposition in general at somewhat lower temperatures than the corresponding silicon compounds (with the exception of the fluoro-derivatives). The thermolysis of $Ph_2CClGeCl_3$ at 150–220°C leads to $Ph_2C{=}CPh_2$, which is probably formed as a result of the dimerisation of the corresponding triplet carbene[268]. Dichlorocarbene, which gives rise to adducts with cyclohexene and cyclo-octene, is formed in the thermolysis of CCl_3GeCl_3 (200–400°C).[268,269] The formation of $:CCl_2$ in the pyrolysis of Cl_3CGeCl_3 has also been demonstrated by the matrix isolation method[270]. Possibly the thermolysis of $CHCl_2GeCl_3$, observed only under severe conditions (700°C) and leading to toluene in the presence of cyclohexene, may also proceed via the carbene pathway[268]. On heating, trifluoromethyltri-iodogermane forms difluorocarbene[271]:

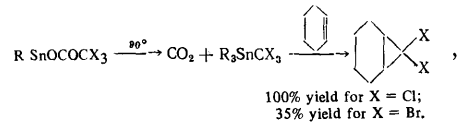


Thermolysis of tri(fluoromethyl)trimethyltin (at 150°C) in the presence of $CF_2{=}CF_2$ leads to perfluorocyclopropane in a quantitative yield[272]. Like the decomposition of trifluoromethyl derivatives of mercury[192–194], this reaction is catalysed by NaI: difluorocarbene adducts are obtained in this way even at 80°C:[273,274]

It is of interest that 2*H*-hexafluorocyclobutyltrimethylstannane is unstable and is converted into pentafluorocyclobutene even at 20°C, evidently via the corresponding carbenopentafluorocyclobutane[275]:

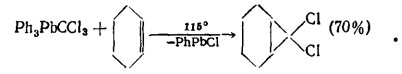
Like the mercury compounds, Me_3SnCCl_2Br and Me_2SnCCl_3 are effective sources of dihalogenocarbenes[276,277]; however, their thermal stability is somewhat greater (the reaction is carried out at 140°C). In contrast to $PhHgCCl_2Br$,[187,188] Me_3SnCCl_2Br gives on thermolysis a certain amount of :CClBr together with $:CCl_2$.[276] The carbene decomposition of dichlorobenzyltrimethylstannane also proceeds under the same conditions[277]:

Thermolysis of compounds of the type $R_3SnOCOCX_3$ (R = alkyl; X = Cl or Br) takes place in two stages[278,279]:

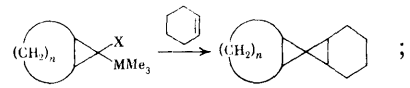


100% yield for X = Cl;
35% yield for X = Br.

Trichloromethyltriphenylplumbane undergoes the carbene decomposition under comparatively mild conditions[280]:



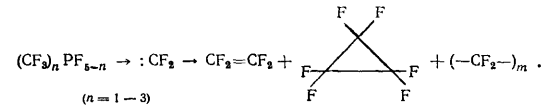
Substituted 1-bromo(iodo)-1-trimethylstannyl and 1-bromo-(iodo)-1-trimethylplumbylcyclopropanes decompose on thermolysis with formation of the corresponding cyclopropylidenes, which are capable of converting olefins into spiropentanes[281]:



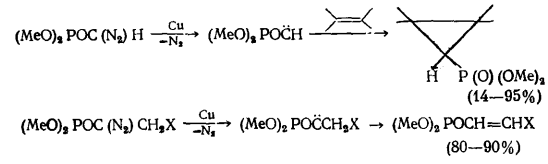
X = Br, or I; M = Sn or Pb.

7. Compounds of Group V Elements

The numerous and widely used methods of synthesis of cyclopropane derivatives from compounds of Group V and VI elements belong to the ylid chemistry and are not the subject of the present review. Few examples of carbene reactions proper have been described for these compounds. Thus thermolysis of $(CF_3)_3Sb$ at 180–220°C and of Ph_2SbCCl_3 at 120°C as well as the decomposition of the unstable $(CCl_3)_3Sb$ proceed, judging from the reaction products, with the intermediate formation of the corresponding dihalogenocarbenes[282,283]. Free difluorocarbene is undoubtedly formed also in the thermolysis of perfluoromethylphosphoranes[284,285]:



α-Dimethylphosphonodiazoalkanes $RC(N_2)PO(OMe)_2$ are thermally extremely stable compounds which decompose under the influence of metallic copper with formation of the corresponding phosphonocarbenes, capable of converting olefins into cyclopropanes or (depending on R) of rearranging to the corresponding unsaturated compounds, for example[286-288]:



Diazo-compounds of the type $Ph_2POC(N_2)R$ (R = H, Ph, $CONH_2$, or COOEt) undergo ultraviolet photolysis to form the carbenes Ph_2POCR, which undergo the Wolff rearrangement, like carbonylcarbenes, leading to $O{=}P(Ph){=}CPhR$; the decomposition of these diazo-compounds under the influence of copper takes place without a rearrangement[289].

8. Carbenes Derived from Transition Metal Compounds

The most characteristic feature of transition metals is their exceptional tendency to fill their vacant atomic orbitals with the electron pairs of ligands; in particular, the occupied molecular orbitals of various organic compounds can play the role of electron pairs. For this reason, organic derivatives of transition metals in which all the coordination vacancies are occupied show the greatest stability. The above condition is satisfied by the carbene complexes of transition metals of the type $(CO)_5MCR(Y)$ (where M = Cr, Mo, or W; Y = OR or NR_2; R = alkyl or aryl), formed when the corresponding hexacarbonyls interact with RLi, this being followed by the methylation or aminomethylation of the adduct $(CO)_5MCR.(OLi)$.[290] Owing to the formation of the normal C–M σ bonds and the coordinate bond involving nitrogen or oxygen p electrons, compounds of this type are quite stable and can dissociate with formation of the nucleophilic carbenes :CYR only at elevated temperatures. Thus $(CO)_5CrCPh.(OMe)$ forms a mixture of stereoisomeric $\alpha\alpha'$-dimethoxystilbenes—dimers of the carbene :CPh(OMe)—only at 135°C.[291] However, the same compound is capable of converting crotonate esters into cyclopropane derivatives even at 80°C and Ph_2SiH_2 into $Ph_2SiHCH(OMe)Ph$ (albeit with a low yield) even at 55°C.[292,293] Under the influence of pyridine, the complex $(CO)_5CrC(OEt)Me$ decomposes at 60°C with the intermediate formation of the carbene :CMe(OEt), which does not, however, form the corresponding cyclopropane derivatives on reaction with olefins and isomerises wholly to methyl vinyl ether[294]. Complexes of the type $(CO)_5MCPh(OMe)$, where M = Cr, Mo, or W, convert the esters of $\alpha\beta$-unsaturated acids into cyclopropane derivatives at 90–140°C and alkyl vinyl ethers are converted into cyclopropanes even at 50°C in the presence of CO under pressure, the isomeric composition of the cyclopropane derivatives formed depending on the nature of the metal[295,296]. On being refluxed with $PhHgCX_3$ in benzene, the complex $(CO)_5Cr(OMe)Ph$ forms mixed dimers of electrophilic and nucleophilic carbenes of the type $Ph(MeO)C{=}CX_2$.[297] The compound $(CO)_5WCPh_2$ converts ethyl vinyl ether at 37°C and isobutene only at 100°C into cyclopropane derivatives[298].

The facts enumerated above undoubtedly show that in the vast majority of cases the transfer of the carbene from its transition metal complex takes place without the formation of the kinetically free carbene and is a consequence of the reaction of the complex with the substrate. This is confirmed by the fact that the chiral complex (–)-(*R*)-$MePrPhP(CO)_4CrPh(OMe)$ reacts with diethyl fumarate to form the optically active 2,3-diethoxycarbonyl-1-methoxy-1-phenylcyclopropane[299].

Several α-chloromethyl compounds of transition metals, which behave as the precursors of the corresponding carbenes like the analogous compounds of other metals, are known. Thus, when $CrBPh_4$ or $(C_6H_6)_2CrBPh_4$ was heated with CCl_4 in the presence of cyclohexene, 7,7-dichloronorcarane was obtained in 50–54% yields. The reaction apparently proceeds with the intermediate formation of the trichloromethyl derivative of chromium $CCl_3CrClBPh_4$.[300] The chloromethyliridium compound $(Ph_3P)_2(CO)IrCH_2Cl$ interacts with styrene to form a mixture of phenylcyclopropane and 2-methylstyrene but is incapable of introducing the methylene group into cyclohexene[301]. In the presence of hydrochloric acid, the iron complex $(\pi\text{-}C_5H_5).(CO)_2FeCH_2OMe$ introduces the methylene group into cyclohexene at 50°C with a high yield; it has been suggested that $(\pi\text{-}C_5H_5)(CO)_2FeCH_2Cl$ is an intermediate in

this reaction. The same methoxymethyl derivative of iron as well as $(\pi\text{-}C_5H_5)(CO)_3MoCH_2OMe$ introduce the methylene group into cyclohexene on treatment with HBF_4 even at 0°C.[302]

Thermolysis of the iridium complexes $(Ph_3P)_2(CO)IrCl.(OCOCF_2Cl)X$, where X = H or CHF_2, proceeds with the elimination of CO_2 and difluorocarbene judging from the formation of compounds of the type $(Ph_3P)_2(CO)IrCl_2X$, but attempts to obtain by this reaction the adducts of difluorocarbene with olefins were unsuccessful[303]. On the other hand, the trifluoromethyl derivative of iron $CF_2Fe(CO)_4I$ decomposes at 100°C, forming difluoro- and perfluorocyclopropanes on reaction with ethylene and tetrafluoroethylene respectively[304].

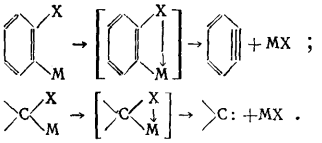
The complex $(CO)_5WCPh_2$, mentioned above, and the analogous chromium complex react with isobutene at 100°C to form not only the corresponding cyclopropane but also (mainly) 1,1-diphenylethylene. The analogous reaction with α-methoxystyrene also gives $CH_2{=}CPh_2$ and the stable complexes $(CO)_5MC(OMe)Ph$. The reaction of the carbonyl complexes of diphenylcarbene with olefins thus proceeds via a redistribution of the fragments of the C=C bond, i.e. is an analogue of the metathesis of olefins[298]. The intermediate involvement of carbene complexes has been recently suggested in the discussion of the mechanism of the metathesis reaction proper[305].

The methylene complex of tantalum $(\pi\text{-}C_5H_5)_2Ta(CH_3).CH_2$, which was synthesised recently[306], disproportionates slowly at 25°C, forming the corresponding ethylene complex $(\pi\text{-}C_5H_5)_2Ta(CH_3)C_2H_4$, but the reaction apparently proceeds without the involvement of free CH_2. It is of interest that the methylene entering into the composition of this complex manifests nucleophilic and not electrophilic properties. According to NMR data, the barrier to the rotation of CH_2 about the Ta–C bond is approximately 20 kcal mole^{-1}.[307]

VI. THE MECHANISM OF THE DECOMPOSITION OF HALOGENO-DERIVATIVES OF ORGANOMETALLIC COMPOUNDS‡

The data presented for the thermal stabilities of *o*-halogenoaryl and α-halogenomethyl derivatives of organometallic compounds demonstrate convincingly that their decomposition with formation of arynes and carbenes proceeds with participation of a vacant orbital of the metal. Indeed, numerous lithium, magnesium, boron, aluminium, zinc, and transition metal compounds are much more stable in the form of their complexes with *n*-donor ligands, which is not observed for compounds of metals with a lone electron-accepting capacity (for example, mercury). The finding that halogeno-derivatives of organic Group I–III elements having vacant *p* orbitals are on the whole much less stable than their analogues formed from elements in Group IV and subsequent Groups is undoubtedly also associated with the involvement of a free metal orbital in the reaction.

On the other hand, analysis of the literature data shows that the reactions under consideration can be readily carried out as single-stage processes only when the second eliminated group contains a free electron pair. The generality of these conclusions suggests that the most probable pathway in the decomposition of organometallic precursors of arynes and carbenes is intramolecular coordination[308,309], being apparently the pathway involving least migration[310]:



This conclusion can evidently be justified theoretically on the basis of the simple theory of molecular orbitals and their interactions, the applicability of which (particularly of the principle of the conservation of the key properties of the molecular orbitals during the reaction[105]) to the related problems of the mechanisms of the reactions of organometallic compounds has been demonstrated recently[311].

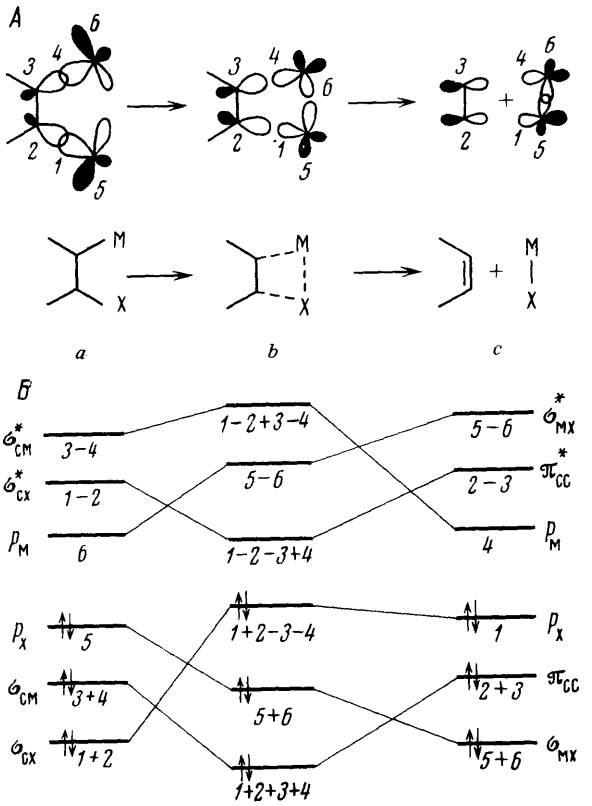


Figure 2. *A*) Changes in the molecular orbitals during the concerted decomposition of vicinal halogeno-derivatives of organometallic compounds [*a*) initial compound; *b*) transition state; *c*) reaction products]; *B*) correlation diagram (after Zimmerman[105]); the numerals on the diagram correspond to the numbering of the atomic orbitals.

It follows from the correlation diagram that the decomposition of vicinal (and similarly also geminal) halogeno-derivatives of organometallic compounds is symmetry-allowed when the coordinating orbitals are the boundary orbitals of the system (Fig. 2). In contrast to this, the

‡This section was written jointly with A.I. Ioffe.

synchronous decomposition of compounds of this type, which proceeds with participation of the molecular orbitals of the C–X and C–H bonds only, is symmetry-forbidden as a (2*s* + 2*s*) cyclodecomposition process[90]. It is quite evident that the characteristics of the reactions considered are consistent with the hypothesis that symmetry-allowed processes take place preferentially.

In considering the factors determining the stability of halogeno-derivatives of organometallic compounds, one must therefore take into account the fact that the activation energies for the decomposition reactions must depend not only on the heat of reaction (according to the Bell–Evans–Polanyi principle but also on a number of factors determining intramolecular coordination: on the energy gap between the molecular orbitals of the donor and acceptor (the *p* orbitals of the halogen and metal atoms respectively), on the distance between the M and X atoms in the molecule of the initial compound, and on the strength of the metal–ligand coordinate bond (when the reaction is carried out in the appropriate solvents). The first two factors determine the position of the transition state on the reaction coordinate, since it is formed sooner (and the activation energy is correspondingly smaller) the greater the sum of the valence radii of the M and X atoms and the smaller the difference between the corresponding orbital ionisation potentials. For this reason, the most important factors determining the stability of the compounds under consideration include their capacity for the formation of associated species, since an extremely effective decrease of the X–M distance is thereby achieved (for example the Li–F distance is 3.3 Å in the C_6H_4LiF monomer, while the corresponding distance in the tetramer having a structure analogous to that of methyl-lithium[312] is only 2.0 Å). The analogous effect should also be observed for dimers and one may therefore expect that associated halogeno-derivatives of organometallic compounds should be less stable (in the presence of a free metal orbital) than the corresponding monomeric compounds.

Owing to the lack of thermochemical data, the correct calculation of the heats of the reactions considered ($Q = D_{MX} + D_{CC} - D_{CM} - D_{CX}$, where D are the heats of dissociation of the corresponding bonds)—undoubtedly the most important factor determining the activation energy—is so far impossible. However, for compounds of a single metal decomposing in the same medium with formation of the same unstable species (for example, the process $o\text{-}XC_6H_4Li \rightarrow LiX + C_6H_4$), the relative heats of reaction (and hence the ratio of the activation energies) for reactions involving different X may be estimated from the differences ΔD between the heats of dissociation of the M–X and C–X bonds. Owing to the lack of the necessary data for the heats of dissociation of the C–M bonds, the effects of various metals in their compounds may be estimated qualitatively using the data for the corresponding M–H bonds, the heats of dissociation of which are usually close to those of the C–M bonds[251]. Only a qualitative allowance for the remaining factors influencing the stability of halogeno-derivatives of organometallic compounds is at present possible.

Since the C–X bond strength is only one of the factors determining the heat of reaction, the attempts to relate the stability of halogeno-derivatives of organometallic compounds to this quantity alone usually do not lead to correct predictions. Virtually the only examples of a satisfactory correlation between D_{CX} and T_d are provided by the compounds $o\text{-}XC_6H_4Li$, whose decomposition temperatures T_d decrease in the following sequence of X: F > Cl > Br,[40] and by $LiCHX_2$ (Cl > Br > I).[133,144,145] However, in these cases too the values of ΔD represent more satisfactorily the sequence in which the temperatures T_d diminish as a function of X (F > Cl > Br) than do the values of D_{CX} (F ≫ Cl > Br). The correlation usually drawn between T_d and the polarity of the C–M bond is inapplicable to thermolytic reactions and comparison of the values of D_{CM} as criteria of the stability of compounds of different metals usually leads to incorrect estimates. Thus the values of D_{CM} for the C–Li and C–Hg bonds are similar [62 kcal mole^{-1} for CH_3Li and 56 kcal mole^{-1} for $(CH_3)_2Hg$[251,313]], while the decomposition temperature T_d of $LiCCl_3$ is lower than that of $C_6H_5HgCCl_3$ by approximately 300°C.[81,188] Much more reasonable correlations are obtained in the analysis of the heats of reaction. Thus the sharp increase of stability observed on passing from alkali metals and magnesium to heavy metal derivatives is associated with a decrease of D_{MX}, so that $\Delta D = 30 - 50$ kcal mole^{-1} (for virtually constant values of D_{CM}).

When the relative stabilities of compounds of more similar metals are considered, one must take into account also the differences between the values of D_{CM}. It follows from the known values of D_{MH} that the differences between the D_{CM} for alkali metal and magnesium compounds should not exceed 10 kcal mole^{-1}. Examination of the values of $\Delta D - D_{MH}$ makes it possible to estimate the heats of the decomposition reactions of the analogous lithium, sodium, potassium, and magnesium compounds, the results showing their extreme similarity; the highest heat and hence the smallest activation energy should be observed for lithium and magnesium compounds, which is usually the case. Thus the decomposition temperatures T_d of the compounds $MCHBr_2$ lie in the sequence Na ≃ MgX > K ≃ Li and those of the compounds MCBr lie in the sequence Na ≃ MgBr > Li ≃ K.[144,161,164] The difference between the heats of reaction of magnesium and lithium compounds, having virtually the same values of ΔD, is determined by the difference between the values of D_{CM}, which (together with the difference between the heats of dissociation of the M–O etherate linkages) probably also determines the relative stabilities of the corresponding trifluoromethyl compounds: $CF_3MgBr \ll CF_3Li$.[142,164,314] One should note that, when an ionic mechanism obtains, the stability should in all cases follow the sequence XMg > Li > Na > K.

The relative stabilities of compounds whose decomposition leads to different molecules are greatly influenced by D_{CC}—the energy of the C–C bond formed in an unstable molecule. In particular, owing to the much smaller energy of the triple bond in cyclopentyne than in cyclohexyne and cycloheptyne, 2-bromo-1-lithiocyclopentene is much more stable than the corresponding six- and seven-membered compounds[31–33,315]. For the same reason, compounds such as 1-lithioperfluoronorbornene[315], halogeno-1,2-dilithioferrocenes[317], and lithio-derivatives of halogenothiophens and furans[318,319] are also stable. D_{CC} for carbenes is equivalent to E_{ST}; according to calculations[88,89], this quantity is a maximum for CF_2 and a minimum for CH_2, while its value for CCl_2 has been estimated as being intermediate[86]. This sequence of values of D_{CC}, which is the reverse of that of ΔD, evidently equalises the decomposition temperatures T_d for $LiCX_3$ (F ≃ Cl ≃ Br)[40,130,142,144] and is the reason why the relative stability of $LiCHCl_2$ is much greater than that of $LiCH_2Cl$.[101,133]

The influence of the distance between the eliminated groups undoubtedly causes the decomposition temperature of $KCBr_3$ to be smaller than that of $NaCBr_3$.[161] In contrast

to monohalogeno-compounds, pentachloro- and pentabromo-phenyl-lithium should be monomeric or should form less strongly bound associated species for steric reasons, as a result of which the halogen–metal distance in these compounds should be greater. In conformity with these considerations, pentachloro- and pentabromo-lithiobenzenes are much more stable than the monohalogeno-compounds.[42,52,53] Stabilisation of this kind is observed also for pentahalogenophenyl Grignard reagents[52,66–70,74,320,321] and for biphenyl[59,60,322], phenyl ether[61], and pyridine[65] derivatives. 2-Bromo-2-lithiobiphenyl, in the stable conformation of which the planes of the benzene rings are mutually perpendicular and the distance between the Li and Br atoms exceeds 4.3 Å, are stable even on boiling in ether[53].

It appears evident that the energetic and structural factors examined are the main ones among those which determine the resistance of halogeno-derivatives of organometallic compounds to carbene or aryne decomposition. At the same time, the correct treatment of this problem must take into account also many other factors, such as the change in bond energy under the influence of substituents, the stability of reaction products, their heats of solvation, etc., which does not appear possible at the present time.

REFERENCES

1. J. Hine, "Divalent Carbon", Ronald Press, New York, 1964.
2. R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes" Acad. Press, New York, 1967.
3. T. L. Gilchrist and C. W. Reese, "Carbenes, Nitrenes and Arynes", Nelson, London, 1969.
4. W. Kirmse, "Carbene Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1967.
5. W. Kirmse, "Carbene Chemistry", Acad. Press, New York, 1971.
6. M. Jones and R. Moss, "Carbenes", Wiley and Sons, New York, 1970, Vol. 1.
7. G. Kobrich, Angew. Chem., 79, 15 (1967); 84, 557 (1972).
8. H. E. Simmons, T. L. Cairns, S. A. Vladuchick, and C. M. Hoiness, in "Organic Reactions", Wiley and Sons, New York, 1973, Vol. 20, p. 1.
9. D. Seyferth, Accounts Chem. Res., 5, 65 (1972).
10. G. Wittig, Naturwiss., 30, 696 (1942).
11. R. S. Berry, J. Clardy, and M. E. Schafer, Tetrahedron Letters, 1003 (1965).
12. M. E. Schafer and R. S. Berry, J. Amer. Chem. Soc., 87, 4499 (1965).
13. R. S. Berry, G. N. Spokes, and M. Styles, J. Amer. Chem. Soc., 84, 3570 (1962).
14. O. L. Chapman, K. Mattes, C. L. McIntosh, J. Pacansky, G. B. Calder, and G. Orr, J. Amer. Chem. Soc., 95, 6134 (1973).
15. E. W. Gowling, S. F. A. Kettle, and G. M. Sharples, Chem. Comm., 21 (1968).
16. R. Hoffmann, A. Imamura, and W. J. Hehre, J. Amer. Chem. Soc., 90, 1499 (1968).
17. J. F. Olsen, J. Mol. Struct., 8, 307 (1971).
18. D. L. Wilhite and J. L. Whitten, J. Amer. Chem. Soc., 93, 2858 (1971).
19. E. Haselbach, Helv. Chim. Acta, 54, 1987 (1971).
20. M. J. S. Dewar and W.-K. Li, J. Amer. Chem. Soc., 96, 5569 (1974).
21. H. T. Gruentzmacher and J. Lohman, Annalen, 705, 81 (1967).
22. R. T. Luibrand and R. W. Hoffmann, J. Org. Chem., 39, 3887 (1974).
23. L. E. Hatch and D. Peter, Chem. Comm., 1499 (1968).
24. R. W. Atkin and C. W. Reese, Chem. Comm., 152 (1969).
25. M. Jones and R. H. Levin, J. Amer. Chem. Soc., 91, 6411 (1969).
26. H. Heaney, K. G. Mason, and J. M. Sketchley, J. Chem. Soc., C, 567 (1971).
27. P. Crews and J. Beard, J. Org. Chem., 38, 522 (1973).
28. L. Lombardo and D. Wege, Tetrahedron Letters, 3981 (1971).
29. H. H. Wasserman, A. J. Solodar, and L. S. Keller, Tetrahedron Letters, 5547 (1968).
30. N. D. Epiotis, J. Amer. Chem. Soc., 95, 1191 (1973).
31. G. Wittig and H.-L. Dorsch, Annalen, 711, 46 (1968).
32. G. Wittig and J. Meske-Schüller, Annalen, 711, 65 (1968).
33. G. Wittig and H. Heyn, Annalen, 726, 57 (1969).
34. G. Wittig and J. Meske-Schüller, Annalen, 711, 76 (1968).
35. W. R. Moore and W. R. Moser, J. Amer. Chem. Soc., 92, 5469 (1970).
36. P. Dillon and C. R. Underwood, J. Amer. Chem. Soc., 96, 779 (1974).
37. R. Hoffmann and D. M. Hayes, J. Phys. Chem., 76, 656 (1972).
38. H. Heaney, F. G. Mann, and I. T. Miller, J. Chem. Soc., 3930 (1957).
39. O. M. Nefedov and A. I. D'yachenko, Izv. Akad. Nauk SSSR, Ser. Khim. (in the Press).
40. H. Gilman and R. D. Gorsich, J. Amer. Chem. Soc., 77, 3919 (1955).
41. O. M. Nefedov and A. I. D'yachenko, Dokl. Akad. Nauk SSSR, 198, 593 (1971).
42. O. M. Nefedov and A. I. D'yachenko, Angew. Chem., 84, 527 (1972).
43. O. M. Nefedov, A. I. D'yachenko, and A. Ya. Shteinshneider, Izv. Akad. Nauk SSSR, Ser. Khim., 1845 (1971).
44. O. M. Nefedov, A. I. D'yachenko, and A. Ya. Shteinshneider, Izv. Akad. Nauk SSSR, Ser. Khim., 320 (1975).
45. H. L. Lewis and T. L. Brown, J. Amer. Chem. Soc., 92, 4664 (1970).
46. I. Haiduc and H. Gilman, J. Organometallic Chem., 12, 394 (1968).
47. S. S. Dua and H. Gilman, J. Organometallic Chem., 64, C1 (1974).
48. C. Tamborsky and E. J. Soloski, J. Organometallic Chem., 20, 245 (1969).

49. C.S.Cohen, D.E.Fenton, D.Show, and A.G.Massey, J.Organometallic Chem., 8, 1 (1967).
50. C.Tamborsky and E.J.Soloski, J.Organometallic Chem., 10, 385 (1967).
51. D.D.Callender, P.L.Coe, and J.C.Tatlow, Tetrahedron, 22, 419 (1966).
52. D.J.Berry and B.J.Wakefield, J.Chem.Soc.C, 2342 (1969); 642 (1971).
53. M.D.Rausch, G.A.Moser, and C.F.Meade, J. Organometallic Chem., 51, 1 (1973).
54. C.Tamborsky and E.J.Soloski, J.Org.Chem., 31, 746 (1966).
55. P.J.Harper, E.J.Soloski, and C.Tamborsky, J. Org.Chem., 29, 2385 (1964).
56. K.Kuroda and N.Ishikava, Nippon Kagaku Zasshi, 91, 989 (1970); Chem.Abs., 73, 6669 (1970).
57. C.Tamborsky and E.J.Soloski, J.Org.Chem., 31, 743 (1966).
58. T.H.Kikstle and J.P.Bechner, J.Organometallic Chem., 22, 497 (1970).
59. R.A.Contigani, H.E.Bertorello, and M.Martinez de Bertorello, J.Organometallic Chem., 32, 7 (1971).
60. C.S.Cohen, H.L.N.Reddy, D.M.Roe, A.J.Tomlinson, and A.G.Massey, J.Organometallic Chem., 14, 241 (1968).
61. R.L.de Pasquale and C.Tamborsky, J.Organometallic Chem., 13, 273 (1968).
62. M.Martinez de Bertorello and H.E.Bertorello, J.Organometallic Chem., 23, 285 (1969).
63. N.J.Foulger and B.J.Wakesfield, J.Organometallic Chem., 69, 161, 321 (1974).
64. P.Claubere and B.Gorny, J.Organometallic Chem., 37, 401 (1972).
65. J.D.Cook and B.J.Wakesfield, J.Organometallic Chem., 13, 15 (1968).
66. H.Heaney and J.M.Yablonsky, Tetrahedron Letters, 4529 (1966).
67. C.Tamborsky and G.J.Moore, J.Organometallic Chem., 26, 153 (1971).
68. G.Wittig and L.Pohmer, Chem.Ber., 89, 1334 (1956).
69. H.Heaney and J.M.Yablonsky, J.Chem.Soc., C, 1895 (1968).
70. C.F.Smith, G.J.Moore, and C.Tamborsky, J. Organometallic Chem., 33, C21 (1971); 42, 257 (1972).
71. S.C.Cohen and A.G.Massey, J.Organometallic Chem., 10, 341 (1968).
72. C.Tamborsky, E.J.Soloski, and J.M.Dec, J. Organometallic Chem., 4, 446 (1966).
73. A.E.Jukes, S.S.Dua, and H.Gilman, J.Organometallic Chem., 21, 241, 24, 701 (1970).
74. V.B.Smith and A.G.Massey, J.Organometallic Chem., 23, C11 (1970).
75. D.M.Roe and A.G.Massey, J.Organometallic Chem., 23, 547 (1970).
76. C.F.Smith and C.Tamborsky, J.Organometallic Chem., 32, 257 (1971).
77. J.L.W.Pohlmann, F.E.Brinkmann, G.Tesi, and R.E.Daraldo, Z.Naturforsch., 20B, 5 (1965).
78. G.B.Deacon and J.C.Parrot, J.Organometallic Chem., 22, 287 (1970).
79. E.Kinsella, V.B.Smith, and A.G.Massey, J. Organometallic Chem., 34, 181 (1972).
80. T.A.George, J.Organometallic Chem., 33, C13 (1971).
81. L.Andrews, J.Chem.Phys., 47, 4834 (1968).
82. A.K.Maltsev, R.G.Mikaelyan, O.M.Nefedov, R.H.Hauge, and J.L.Margrave, Proc.Nat.Acad. Sci., 68, 3238 (1971).
83. O.M.Nefedov and A.I.Ioffe, Zhur.Vses.Khim. Obshch.im.Mendeleeva, 19, 305 (1974).
84. A.K.Mal'tsev, Symposium, "Novoe v Khimii Karbenov" (Advances in Carbene Chemistry), Izd. Akad.Nauk SSSR, Moscow, 1973.
85. J.F.Harrison, Accounts Chem.Res., 7, 378 (1974).
86. R.Hoffmann, G.D.Zeiss, and G.W.Van Dine, J. Amer.Chem.Soc., 90, 1485 (1968).
87. R.Gleiter and R.Hoffmann, J.Amer.Chem.Soc., 90, 5457 (1968).
88. J.F.Harrison, J.Amer.Chem.Soc., 93, 4112 (1971).
89. V.Staemmler, Theor.Chim.Acta, 35, 309 (1974).
90. R.B.Woodward and R.Hoffmann, "The Conservation of Orbital Symmetry" (Translated into Russian), Izd.Mir, Moscow, 1971.
91. N.Bodor, M.J.S.Dewar, and J.S.Wasson, J.Amer. Chem.Soc., 94, 9095 (1972).
92. R.Hoffmann, J.Amer.Chem.Soc., 90, 1475 (1968).
93. R.Hoffmann, D.M.Hayes, and P.S.Skell, J.Phys. Chem., 76, 664 (1972).
94. P.S.Skell and R.G.Woodworth, J.Amer.Chem.Soc., 78, 4496 (1956).
95. G.L.Closs and L.E.Closs, Tetrahedron Letters, 38 (1960).
96. W.von E.Doering and L.H.Knox, J.Amer.Chem. Soc., 72, 2305 (1950).
97. M.E.Vol'pin, V.G.Dulova, and D.N.Kirsanov, Dokl.Akad.Nauk SSSR, 128, 951 (1959).
98. O.M.Nefedov, N.N.Novitskaya, and A.D.Petrov, Dokl.Akad.Nauk SSSR, 158, 411 (1964).
99. R.Hoffmann, R.Gleiter, and F.B.Mallory, J. Amer.Chem.Soc., 92, 1460 (1968).
100. H.Hoberg, Annalen, 656, 1 (1962).
101. G.Köbrich and R.H.Fischer, Tetrahedron, 24, 4343 (1968).
102. R.Huisgen and U.Burger, Tetrahedron Letters, 3049 (1970).
103. L.Friedman, R.J.Honour, and J.G.Berger, J. Amer.Chem.Soc., 92, 4640 (1970).
104. E.P.Blanchard and H.E.Simmons, J.Amer.Chem. Soc., 86, 1337 (1964).
105. H.E.Zimmerman, Accounts Chem.Res., 5, 393 (1972).
106. S.Arora and P.Binger, Synthesis, 801 (1974).
107. L.Skattebol, Acta Chim.Scand., 17, 1683 (1965).
108. P.Le Parchee and J.M.Conia, Tetrahedron Letters, 1587 (1970).
109. N.Bodor and M.J.S.Dewar, J.Amer.Chem.Soc., 94, 9103 (1972).
110. N.Bodor, M.J.S.Dewar, and Z.B.Maksic, J. Amer.Chem.Soc., 95, 5245 (1973).
111. B.M.Trost and M.J.Bogdanovich, J.Amer.Chem. Soc., 95, 5307 (1973).
112. O.M.Nefedov and A.A.Ivashenko, Izv.Akad.Nauk SSSR, Ser.Khim., 2209 (1965).
113. P.B.Reinarts and G.J.Fohnen, Tetrahedron Letters, 4013 (1973).
114. D.W.Brown, M.E.Hendrick, and M.Jones, Tetrahedron Letters, 3951 (1973).
115. D.P.G.Hamon and V.C.Trennery, Tetrahedron Letters, 1971 (1974).
116. M.S.Baird, Chem.Comm., 1145 (1971).
117. H.Nosaki, T.Aratani, T.Toraya, and R.Noyori, Tetrahedron Letters, 905 (1971).
118. G.Kobrich, H.Trapp, and I.Hornke, Chem.Ber., 100, 961 (1967).

119. G. Kobrich, G. Reitz, and U. Schumacher, Chem. Ber., 105, 1674 (1972).
120. G. Wittig and H. Witt, Ber., 74, 1474 (1941).
121. G. Wittig and U. Pockels, Ber., 72, 884 (1939).
122. A. Lepley and R. L. London, J. Amer. Chem. Soc., 91, 748 (1969).
123. H. R. Ward, R. G. Lowler, and R. A. Cooper, J. Amer. Chem. Soc., 91, 746 (1969).
124. P. D. Bartlett, C. W. Goebel, and W. P. Weber, J. Amer. Chem. Soc., 91, 7425 (1969).
125. G. L. Closs and J. J. Coyle, J. Org. Chem., 31, 2759 (1966).
126. G. Kobrich and R. H. Fischer, Chem. Ber., 101, 3208 (1968).
127. O. M. Nefedov and V. I. Shiryaev, Zhur. Obshch. Khim., 37, 1223 (1967).
128. R. H. Fischer and G. Kobrich, Chem. Ber., 101, 3230 (1968).
129. O. M. Nefedov and A. I. D'yachenko, Izv. Akad. Nauk SSSR, Ser. Khim., 487 (1972).
130. G. Kobrich, H. R. Merkie, K. Flory, and R. H. Fischer, Chem. Ber., 99, 1793 (1966).
131. R. Huisgen and U. Burger, Tetrahedron Letters, 3053 (1970).
132. G. L. Closs and L. E. Closs, J. Amer. Chem. Soc., 82, 5723 (1960).
133. D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, J. Amer. Chem. Soc., 87, 4247 (1965).
134. O. M. Nefedov, V. I. Shiryaev, and A. D. Petrov, Zhur. Obshch. Khim., 32, 662 (1962).
135. D. Seyferth and R. L. Lampert, J. Organometallic Chem., 55, C53 (1973).
136. G. Kobrich and W. Goyert, Tetrahedron, 24, 4327 (1968).
137. O. M. Nefedov, A. A. Ivashenko, M. N. Manakov, V. I. Shiryaev, and A. D. Petrov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 367 (1962).
138. O. M. Nefedov and A. A. Ivashenko, Dokl. Akad. Nauk SSSR, 156, 884 (1964).
139. J. Villieras, C. Saquet, D. Masura, and J. F. Normant, J. Organometallic Chem., 50, C7 (1973).
140. G. Kobrich and R. H. Fischer, Chem. Ber., 101, 3219 (1968).
141. G. Kobrich and F. Ansari, Chem. Ber., 100, 2011 (1967).
142. T. V. Talaeva and K. A. Kocheshkov, "Metody Elementoorganicheskoi Khimii. Litii, Natrii, Kalii, Rubidii, Tsezii" (Methods of Organoelement Chemistry. Lithium, Sodium, Potassium, Rubidium, and Caesium), Izd. Nauka, Moscow, 1971, Vol. 1, p. 182.
143. G. Kobrich and H. R. Merkle, Chem. Ber., 99, 1782 (1966).
144. R. H. Fischer and G. Kobrich, Chem. Ber., 101, 3230 (1968).
145. G. Kobrich and R. von Nagel, Chem.-Ztg., 94, 984 (1970).
146. D. Seyferth and R. L. Lambert, J. Organometallic Chem., 54, 123 (1973).
147. A. I. D'yachenko and O. M. Nefedov, Symposium, "Novoe v Khimii Karbenov" (Advances in Carbene Chemistry), Izd. Akad. Nauk SSSR, Moscow, 1973.
148. P. S. Skell and M. S. Cholod, J. Amer. Chem. Soc., 91, 7131 (1969).
149. K. G. Taylor, W. E. Hobbs, and M. Saquet, J. Org. Chem., 36, 369 (1971).
150. O. M. Nefedov and R. N. Shafran, Izv. Akad. Nauk SSSR, Ser. Khim., 538 (1965).
151. M. Schlosser and Le Van Chau, Angew. Chem., 83, 150 (1971).
152. R. D. Chambers, W. K. Musgrave, and J. Savory, J. Chem. Soc., 1993 (1962).
153. G. Kobrich, H. Trapp, and I. Hornke, Tetrahedron Letters, 1135 (1964).
154. G. Kobrich and N. Trapp, Chem. Ber., 99, 670 (1966).
155. A. Stein and T. H. Morton, Tetrahedron Letters, 4933 (1973).
156. M. Makosza and M. Wawerzyniewiez, Tetrahedron Letters, 4659 (1969).
157. M. Braun and D. Seebach, Angew. Chem., 86, 279 (1974).
158. D. Seyferth, E. M. Hanson, and F. H. Amberlecht, J. Organometallic Chem., 23, 361 (1970).
159. D. Seyferth, R. A. Lambert, and E. M. Hanson, J. Organometallic Chem., 24, 647 (1970).
160. C. M. Warner and J. G. Noltes, J. Organometallic Chem., 24, C4 (1970).
161. B. Martel and J. M. Hiriart, Tetrahedron Letters, 2737 (1971).
162. B. Martel and J. M. Hiriart, Synthesis, 201 (1972).
163. J. Villieras and H. Normant, Bull. Soc. chim. France, 1520 (1967).
164. J. Villieras, J. Organometallic Chem., 34, 209 (1972).
165. M. Davies, L. M. Deady, A. J. Finch, and J. F. Smith, Tetrahedron, 29, 349 (1973).
166. H. E. Simmons and R. D. Smith, J. Amer. Chem. Soc., 80, 5323 (1958).
167. H. E. Simmons and R. D. Smith, J. Amer. Chem. Soc., 81, 4256 (1959).
168. R. C. Neumann, Tetrahedron Letters, 2541 (1964).
169. E. Le Goff, J. Org. Chem., 29, 2048 (1964).
170. R. J. Rowson and I. T. Harrisson, J. Org. Chem., 35, 2057 (1970).
171. J. M. Denis, C. Girard, and J. M. Conis, Synthesis, 549 (1972).
172. J. Furukawa, N. Kawabata, and J. Nishimura, Tetrahedron Letters, 3495 (1968), 3353 (1966).
173. J. Nishimura and J. Furukawa, Chem. Comm., 1375 (1971).
174. S. Miyano and H. Hashimoto, Bull. Chem. Soc. Japan, 47, 1500 (1974).
175. S. Miyano, Y. Matsumoto, and H. Hashimoto, Chem. Comm., 364 (1975).
176. R. F. Galliulina, G. G. Petukhov, V. I. Khrulev, and Yu. N. Krasnov, Zhur. Obshch. Khim., 44, 1978 (1974).
177. S. Miyano and H. Hashimoto, Bull. Chem. Soc. Japan, 46, 892 (1973).
178. G. Wittig and K. Schwarzenbach, Angew. Chem., 71, 652 (1959).
179. G. Wittig and K. Schwarzenbach, Annalen, 650, 1 (1961).
180. G. Wittig and F. Winkler, Chem. Ber., 97, 2146 (1964).
181. G. Wittig and H. Jantelat, Annalen, 702, 24 (1967).
182. S. H. Goh, L. E. Closs, and G. L. Closs, J. Org. Chem., 34, 25 (1969).
183. L. Y. Goh and S. H. Goh, J. Organometallic Chem., 23, 5 (1970).
184. D. Bethell and H. C. Brown, Chem. Comm., 1266 (1967).
185. J. Furukawa, N. Kawabata, and T. Fujita, Tetrahedron, 26, 243 (1970).
186. V. I. Shcherbakov, R. F. Galliulina, Yu. N. Krasnov, and V. N. Pankratov, Zhur. Obshch. Khim., 41, 2043 (1970).

187. D.Seyferth, J.Y.-P.Mui, and J.M.Burlitch, J. Amer.Chem.Soc., 89, 4953 (1967).
188. D.Seyferth, J.M.Burlitch, R.J.Minasz, J.Y.-P.Mui, H.D.Simmons, A.J.-H.Treiber, and S.R.Dowd, J.Amer.Chem.Soc., 87, 4259 (1965).
189. D.Seyferth, J.Y.-P.Mui, and R.Damrauer, J. Amer.Chem.Soc., 90, 6182 (1968).
190. V.I.Shcherbakov, Zhur.Obshch.Khim., 41, 1095 (1971).
191. D.Seyferth and C.K.Haas, J.Organometallic Chem., 46, C33 (1972).
192. D.Seyferth and S.P.Hopper, J.Org.Chem., 37, 4070 (1972).
193. D.Seyferth, S.P.Hopper, and K.V.Darragh, J. Amer.Chem.Soc., 91, 6536 (1969).
194. D.Seyferth and S.P.Hopper, J.Organometallic Chem., 26, C62 (1971).
195. D.Seyferth, M.E.Gordon, J.Y.-P.Mui, and J.M.Burlitch, J.Amer.Chem.Soc., 89, 959 (1967).
196. D.Seyferth, M.A.Eisert, and L.J.Todd, J.Amer. Chem.Soc., 86, 121 (1964).
197. D.Seyferth and C.K.Haas, J.Organometallic Chem., 39, C41 (1972).
198. R.Sheffield and U.Michel, Angew.Chem., 80, 160 (1972).
199. D.Seyferth, H.D.Simmons, and H.-M.Shih, J. Organometallic Chem., 29, 359 (1969).
200. D.Seyferth, S.B.Andrews, and H.D.Simmons, J.Organometallic Chem., 17, 9 (1969).
201. D.Seyferth and R.A.Woodruff, J.Organometallic Chem., 71, 335 (1974).
202. T.J.Logan, J.Org.Chem., 28, 1129 (1963).
203. D.Seyferth and C.K.Haas, J.Organometallic Chem., 30, C38 (1972).
204. R.Robson and I.E.Dickson, J.Organometallic Chem., 15, 7 (1968).
205. D.Seyferth, C.K.Haas, and S.P.Hopper, J.Organometallic Chem., 33, C1 (1971).
206. D.Seyferth and K.V.Darragh, J.Org.Chem., 35, 1297 (1970).
207. D.Seyferth and S.P.Hopper, J.Organometallic Chem., 51, 77 (1973).
208. D.Seyferth and D.C.Mueller, J.Amer.Chem.Soc., 93, 3724 (1971).
209. D.Seyferth and D.C.Mueller, J.Organometallic Chem., 25, 293 (1970).
210. N.G.Johansson, Acta Chim.Scand., 27, 1417 (1973).
211. N.G.Johansson and B.Akermark, Acta Chim. Scand., 25, 1927 (1971).
212. D.Seyferth, R.A.Woodruff, D.C.Mueller, and R.L.Lambert, J.Organometallic Chem., 43, 55 (1972).
213. D.Seyferth and R.A.Woodruff, J.Org.Chem., 38, 4031 (1973).
214. D.Seyferth and E.M.Hanson, J.Amer.Chem.Soc., 90, 2438 (1968).
215. D.Seyferth, J.K.Heeren, G.Singh, S.O.Grim, and W.B.Hughes, J.Organometallic Chem., 5, 267 (1966).
216. D.Seyferth, R.M.Turkel, M.A.Eisert, and L.J.Todd, J.Amer.Chem.Soc., 91, 5027 (1969).
217. D.Seyferth and E.M.Hanson, J.Organometallic Chem., 27, 19 (1971).
218. D.Seyferth, S.B.Andrews, and R.L.Lambert, J.Organometallic Chem., 37, 69 (1972).
219. J.A.Langrebe and R.D.Mathis, J.Amer.Chem. Soc., 86, 524 (1964).
220. J.A.Langrebe and R.D.Mathis, J.Amer.Chem. Soc., 83, 3552 (1966).
221. D.C.Mueller and D.Seyferth, J.Amer.Chem.Soc., 91, 1754 (1969).
222. D.Seyferth and D.C.Mueller, J.Organometallic Chem., 28, 325 (1971).
223. O.M.Nefedov and A.A.Ivashchenko, Izv.Akad. Nauk SSSR, Ser.Khim., 446 (1968).
224. A.K.Mal'tsev, R.G.Mikaelyan, and O.M.Nefedov, Izv.Akad.Nauk SSSR, Ser.Khim., 199 (1971).
225. A.K.Mal'tsev, R.G.Mikaelyan, and O.M.Nefedov, Dokl.Akad.Nauk SSSR, 201, 901 (1971).
226. O.M.Nefedov, A.K.Mal'tsev, and R.G.Mikhaelyan, Tetrahedron Letters, 4125 (1971).
227. A.K.Mal'tsev, O.M.Nefedov, R.H.Hauge, J.L.Margrave, and D.Seyferth, J.Phys.Chem., 75, 3984 (1971).
228. R.G.Mikaelyan, Candidate's Thesis, Institute of General Chemistry, USSR Academy of Sciences, Moscow, 1971.
229. A.K.Mal'tsev, N.D.Kagramanov, and O.M.Nefedov, Izv.Akad.Nauk SSSR, Ser.Khim., 1993, 2146 (1974).
230. A.K.Mal'tsev, N.D.Kagramanov, and O.M.Nefedov, Dokl.Akad.Nauk SSSR, 224, 630 (1975).
231. T.Sakakibara, Y.Odaira, and S.Tsutsumi, Tetrahedron Letters, 503 (1968).
232. P.S.Skell and S.J.Valenty, J.Amer.Chem.Soc., 95, 5042 (1973).
233. P.S.Skell, S.J.Valenty, and P.W.Humer, J. Amer.Chem.Soc., 95, 5041 (1973).
234. S.J.Valenty and P.S.Skell, J.Org.Chem., 38, 3937 (1973).
235. O.P.Strausz, T.DoMinh, and J.Font, J.Amer. Chem.Soc., 90, 1930 (1968).
236. T.DoMinh, H.E.Gunning, and O.P.Strausz, J. Amer.Chem.Soc., 89, 6785 (1967).
237. O.P.Strausz, G.J.A.Kennepohl, F.X.Garneau, T.DoMinh, B.Kim, S.J.Valenty, and P.S.Skell, J.Amer.Chem.Soc., 96, 5723 (1974).
238. T.D.Parsons, J.M.Self, and L.H.Schaad, J.Amer. Chem.Soc., 89, 3446 (1967).
239. D.Seyferth and B.Prokai, J.Amer.Chem.Soc., 88, 1834 (1966).
240. H.Hoberg, Angew.Chem., 73, 114 (1961).
241. H.Hoberg, Annalen, 656, 15 (1962).
242. D.B.Miller, Tetrahedron Letters, 989 (1964).
243. J.W.Colette, J.Org.Chem., 28, 2489 (1963).
244. W.Lind and I.J.Worrall, Inorg.Nuclear Chem. Letters, 7, 1153 (1971).
245. V.I.Shcherbakov and S.F.Zhil'tsov, Symposium, "Novoe v Khimii Karbenov" (Advances in Carbene Chemistry), Izd.Akad.Nauk SSSR, Moscow, 1973, p.162.
246. V.I.Shcherbakov and S.F.Zhil'tsov, Zhur.Obshch. Khim., 40, 2046 (1970).
247. W.I.Bevan, R.N.Haszeldine, and J.C.Young, Chem.Ind.(London), 789 (1961).
248. E.Lee and D.W.Roberts, J.Chem.Soc., Perkin Trans., II, 437 (1973).
249. O.M.Nefedov, A.K.Mal'tsev, and V.A.Svyatkin, Izv.Akad.Nauk SSSR, Ser.Khim., 958 (1974).
250. K.G.Sharp and T.D.Koyle, J.Fluor.Chem., 1, 249 (1971/1972).
251. V.N.Kondrat'ev (Editor), "Energii Razryva Khimicheskikh Svyazei, Potentsialy Ionizatsii i Srodstvo k Elektronu" (Chemical Bond Dissociation Energies, Ionisation Potentials, and Electron Affinities), Izd.Nauka, Moscow, 1974.

252. J.M. Bellama and A.G. McDiarmid, J. Organometallic Chem., 18, 275 (1969).
253. T.N. Bell, R.N. Haszeldine, M.J. Newlands, and J.B. Plumb, J. Chem. Soc., 2107 (1965).
254. G. Fishwick, R.N. Haszeldine, C. Parkinson, P.J. Robinson, and R.F. Simmons, Chem. Comm., 382 (1965).
255. D. Seyferth, G.J. Murphy, and R.A. Woodruff, J. Organometallic Chem., 92, 7 (1975).
256. W.I. Bevan, R.N. Haszeldine, J. Midleton, and A.E. Tipping, J. Organometallic Chem., 23, C17 (1970).
257. A.G. Brook and P.J. Dillon, Canad. Chem., 47, 4347 (1969).
258. W.H. Atwell, D.R. Weynberg, and J.G. Uhlmann, J. Amer. Chem. Soc., 91, 2025 (1969).
259. P.S. Skell and E.J. Goldstein, J. Amer. Chem. Soc., 86, 1442 (1964).
260. I.A. D'yakonov, I.B. Repinskaya, and G.V. Golodnikov, Zhur. Obshch. Khim., 35, 199 (1965).
261. R.F. Cunico and Y.-K. Han, J. Organometallic Chem., 81, C9 (1974).
262. D. Seyferth, A.W. Dow, H. Menzel, and T.C. Flood, J. Amer. Chem. Soc., 90, 1080 (1968).
263. W. Ando, A. Sekiguchi, T. Higiwara, and T. Migita, Chem. Comm., 372 (1974).
264. U. Schollkopf and N. Rieber, Angew. Chem., Int. Ed., 6, 884 (1967).
265. U. Schollkopf, B. Banhidai, and H.-U. Scholz, Annalen, 761, 137 (1972).
266. A.G. Brook and J.M. Duff, J. Amer. Chem. Soc., 89, 454 (1967).
267. A.G. Brook, P. Pearce, and J.B. Pierce, Canad. J. Chem., 49, 1622 (1971).
268. S.P. Kolesnikov, B.L. Perl'mutter, and O.M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 1418 (1973).
269. M. Massol, J. Barrau, and J. Satge, Inorg. Nuclear Chem. Letters, 7, 895 (1971).
270. O.M. Nefedov and A.K. Mal'tsev, "XI Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii, Referaty Soobshchenii" (The XIth Mendeleev Congress on General and Applied Chemistry. Abstracts of Communications), Izd. Nauka, Moscow, 1975, Vol. 3, p. 183.
271. H.C. Clark and C.J. Willis, J. Amer. Chem. Soc., 84, 898 (1962).
272. H.C. Clark and C.J. Willis, J. Amer. Chem. Soc., 82, 1888 (1960).
273. D. Seyferth, J.Y.-P. Mui, M.F. Gordon, and J.M. Burlitch, J. Amer. Chem. Soc., 87, 681 (1965).
274. D. Seyferth, H. Dertouzos, R. Suzuki, and J.Y.-P. Mui, J. Org. Chem., 32, 2980 (1967).
275. W.R. Cullen and G.E. Styan, J. Organometallic Chem., 6, 633 (1966).
276. D. Seyferth, F.M. Ambrecht, B. Prokai, and R.J. Cross, J. Organometallic Chem., 6, 573 (1966).
277. D. Seyferth and F.M. Ambrecht, J. Amer. Chem. Soc., 91, 2616 (1969).
278. D. Seyferth, B. Prokai, and R.J. Cross, J. Organometallic Chem., 13, 169 (1968).
279. F.M. Ambrecht, W. Tronich, and D. Seyferth, J. Amer. Chem. Soc., 91, 3218 (1969).
280. C.M. Warner and J.C. Noltes, J. Organometallic Chem., 24, C4 (1969).
281. D. Seyferth and R.L. Lambert, J. Organometallic Chem., 91, 31 (1975).
282. P.B. Ayscough and H.J. Emeleus, J. Chem. Soc., 3381 (1954).
283. R. Muller, S. Reichel, and C. Dathe, J. Prakt. Chem., 311, 930 (1969).
284. W. Mahler, J. Amer. Chem. Soc., 84, 4600 (1962).
285. W. Mahler, Inorg. Chem., 2, 230 (1963).
286. D. Seyferth, P. Hilbert, and R.S. Marmor, J. Amer. Chem. Soc., 89, 4811 (1967).
287. D. Seyferth, R.S. Marmor, and P. Hilbert, J. Org. Chem., 36, 1379 (1971).
288. R.S. Marmor and D. Seyferth, J. Org. Chem., 36, 128 (1971).
289. M. Regitz, A. Liedhegener, W. Anschutz, and H. Eckes, Chem. Ber., 104, 2177 (1971).
290. D.J. Cardin, B. Cetinkaya, and M.F. Lappert, Chem. Rev., 72, 545 (1972).
291. E.O. Fischer, B. Heckl, K.H. Dötz, J. Müller, and H. Werner, J. Organometallic Chem., 16, P29 (1969).
292. E.O. Fischer and K.H. Dötz, Chem. Ber., 103, 1273 (1970).
293. E.O. Fischer and K.H. Dötz, J. Organometallic Chem., 36, C4 (1972).
294. E.O. Fischer and A. Maasbol, J. Organometallic Chem., 12, P15 (1968).
295. K.H. Dötz and E.O. Fischer, Chem. Ber., 105, 1356 (1972).
296. E.O. Fischer and K.H. Dötz, Chem. Ber., 105, 3966 (1972).
297. A. Derenzi and E.O. Fischer, Inorg. Chem. Acta, 8, 185 (1974).
298. C.P. Casey and T.J. Burkhart, J. Amer. Chem. Soc., 96, 7808 (1974).
299. M.D. Cooke and E.O. Fischer, J. Organometallic Chem., 56, 279 (1973).
300. S.F. Zhil'tsov, A.A. Koksharova, and G.G. Petukhov, Symposium, "Novoe v Khimii Karbenov" (Advances in Carbene Chemistry), Izd. Akad. Nauk SSSR, Moscow, 1973, p. 165.
301. F. Mango and I. Dvoretzky, J. Amer. Chem. Soc., 88, 1654 (1966).
302. P.W. Jolly and R. Pettit, J. Amer. Chem. Soc., 88, 5044 (1966).
303. A.J. Schultz, J. McArdle, G.P. Khare, and H. Eisenberg, J. Organometallic Chem., 72, 415 (1974).
304. R.B. King, S.L. Stafford, P.M. Treichel, and F.G.A. Stone, J. Amer. Chem. Soc., 83, 2604 (1967).
305. K.L. Makovetskii, "XI Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii, Referati Soobshchenii" (The XIth Mendeleev Congress on General and Applied Chemistry. Abstracts of Communications), Izd. Nauka, Moscow, 1975, Vol. 2, p. 138.
306. R.R. Schrook, J. Amer. Chem. Soc., 97, 6577 (1975).
307. L.G. Guggenberger and R.R. Schrook, J. Amer. Chem. Soc., 97, 6578 (1975).
308. A.K. Prokof'ev, V.I. Bregadze, and O.Yu. Okhlobystin, Uspekhi Khim., 39, 412 (1970) [Russ. Chem. Rev., No. 3 (1970)].
309. A.K. Prokof'ev, Uspekhi Khim., 45, 1029 (1976) [Russ. Chem. Rev., No. 6 (1976)].
310. O.S. Tee and K. Yates, J. Amer. Chem. Soc., 91, 3074 (1972).
311. A.I. Ioffe, A.I. D'yachenko, and O.M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 1902 (1975).
312. E. Weiss and G. Henken, J. Organometallic Chem., 21, 265 (1970).
313. T. Holm, J. Organometallic Chem., 77, 27 (1974).

314. H.J.Emeleus, J.Chem.Soc., 2979 (1954).
315. G.Wittig and J.Heyn, Annalen, 756, 1 (1972).
316. R.Stephens, J.C.Tatlow, and K.N.Wood, J. Fluorine Chem., 1, 165 (1972).
317. D.B.Slocum, B.P.Koonsvitsky, and C.R.Ernst, J.Organometallic Chem., 38, 125 (1972).
318. G.Wittig and M.Rings, Annalen, 719, 127 (1968).
319. J.Srogl, M.Janda, I.Stibor, and H.Prochaskova, Z.Chem., 464 (1971).
320. D.J.Berry, J.D.Cook, and B.J.Wakesfield, Chem. Comm., 1273 (1969).
321. C.Tamborski and G.J.Moore, J.Organometallic Chem., 26, 253 (1971).
322. S.C.Cohen, D.Moore, R.Price, and A.G.Massey, J.Organometallic Chem., 12, P36 (1968).

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