CARBENES. REACTIVE INTERMEDIATES CONTAINING DIVALENT CARBON

EFTHIMIOS CHINOPOROS

Oscar Fisher Company, Inc., Newburgh, New York

CONTENTS

I. INTRODUCTION

Many attempts have been made in the past to prepare compounds in which the oxygen of carbon monoxide is replaced by two univalent elements or groups of atoms. Although the formation and isolation of such compounds was unsuccessful, nevertheless, their existence was assumed as intermediate products in chemical reactions (9, 89, 125). It was not until modern experimental technique became available, that the possibility of the existence of such species could be proved as intermediates in reaction mechanisms.* These divalent-carbon species bearing no formal charge, are either methylene, or derivatives of methylene known as car-

benes. It is apparent that the carbenes with a sextet of electrons on the divalent carbon could be regarded as bases conjugate to carbonium ions.
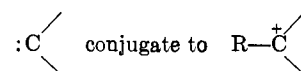
However, in the presence of other molecules they react as electrophilic reagents, attacking nucleophilic centers.

The term "carbene" bears the same relationship to "methylene" as does the term "carbinol" to "methanol" and is employed in the same way as "carbinol." The paired or unpaired condition of the two free electrons on the divalent carbon has been the subject of ex-

* NOTE ADDED IN PROOF.—Not only the intermediate existence of carbenes has been proven, but the isolation of a compound which has been called a stable carbene was achieved. It is now recognized that this carbene is
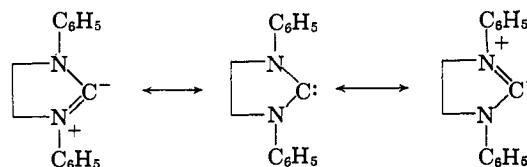
stabilized through carbene-zwitterion resonance, and is in equilibrium with its dimer, as shown by molecular weight determinations; see H. Wanzlick and E. Schikova, *Angew. Chem.*, **72**, 494 (1960).

tensive research, and it is not yet very certain in what electronic state the carbenes exist.

The following pages are concerned with the general methods of formation and the reactions of carbenes, as well as their use. Emphasis is placed mainly on the developments during the period 1950 to the end of 1961.
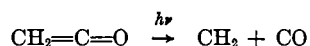
II. METHYLENE

A. PREPARATION

Methylene, the parent compound of carbenes, was first prepared by both the thermal (102) and the photochemical (99) decomposition of diazomethane

$$CH_2N_2 \rightarrow CH_2 + N_2$$

and by the photochemical decomposition of ketene (10, 99)

$$CH_2=C=O \xrightarrow{h\nu} CH_2 + CO$$

in a quartz vessel, and under very low pressures.

The diazomethane required for the reactions is prepared by a variety of methods, of which the most convenient probably is the reaction of methylamine hydrochloride with urea. On reaction with nitrous acid, methylurea is transformed to nitrosomethylurea, which under the action of potassium hydroxide forms diazomethane.

Ketene is prepared by the pyrolysis of either acetone or acetic anhydride, either alone or in the presence of metallic catalysts.

Diazomethane contains the so-called aliphatic diazo group $>CN_2$, and is best represented as a resonance hybrid

$$H_2C=\overset{+}{N}=\overset{-}{N}: \leftrightarrow H_2\overset{-}{C}-\overset{+}{N}\equiv N:$$
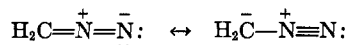
During the displacement of nitrogen to form methylene, diazomethane appears to react as

$$H_2\overset{-}{C}-\overset{+}{N}\equiv N: \rightarrow :CH_2 + N_2$$
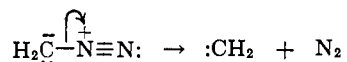
The preparation of methylene by the thermal decomposition of hydrocarbons showed that trivalent carbon radicals are the primary products. Even in the case of the decomposition of diazomethane and ketene, in which methylene is the main product, it passes readily into the trivalent state (101).

Methylene has been prepared also by the reaction of sodium vapor with dibromomethane (8). The reaction takes place in two steps.

$$CH_2Br_2 + Na \rightarrow \cdot CH_2Br + NaBr$$
$$\cdot CH_2Br + Na \rightarrow CH_2 + NaBr$$
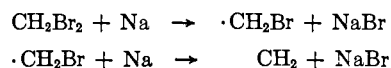
The second step is accompanied by luminescence corresponding to the D line of sodium. The luminescence is produced by the transition of the carbon atom from the quadrivalent to the divalent state.

Although there is not conclusive evidence for the formation of methylene in the reaction of methylene iodide and a zinc–copper couple, the formation of cyclopropanes in the presence of olefins may be considered due to the intermediacy of methylene (26, 114). It is known that the reaction of methylene iodide and zinc–copper couple in dry ether forms iodomethylzinc iodide (31). There are two alternatives for the formation of the cyclopropanes. The iodomethylzinc iodide is regarded as a fairly stable complex of methylene and zinc iodide
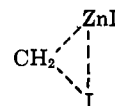

in which the carbon atom is electrophilic, and either zinc iodide is lost spontaneously to give a low energy methylene, or the π-bond of the olefin displaces zinc iodide to produce the cyclopropane (114).
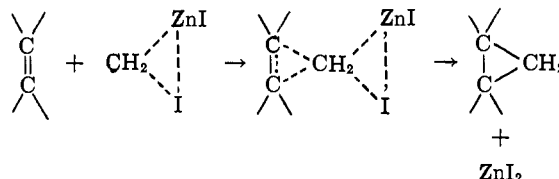
The half-life of methylene varies with the nature of the carrier gas and is as long as 0.23 sec. in nitrogen at about 1.5 mm. pressure (99). The variation of the half-life of methylene is attributed to its reactions with the carrier gas. For instance, methylene reacts with carbon monoxide to form ketene (20, 67), which then in the presence of methylene produces carbon monoxide and ethylene (68). On the other hand, methylene does not add on to nitrogen to reverse the photodissociation of diazomethane (20).

B. STRUCTURE

Although a considerable amount of research has been done on the determination of both the electronic and geometrical configuration of methylene, its structure has not as yet been established in a clear manner. Contradictory statements have been given as to whether methylene is in the singlet state (Ia), having sp² hybridization, or in the triplet state (Ib), having the structure of a biradical.
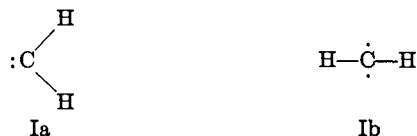
A variety of methods has been tried to solve the problem of the ground state of methylene. One of these attempts was to correlate the stability of methylene with that of the methyl radical. A higher stability

for methylene than that for the methyl radical is associated with the singlet state, while a lower stability occurs with the triplet state. The stabilities of methylene and methyl radical are judged on the basis of the dissociation energies E of the CH–H and CH_2–H bonds, obtained from electron impact studies on methane, methyl radical and methylene. In Table I are given the dissociation energies of the two species as obtained by different investigators.

TABLE I

DISSOCIATION ENERGIES OF CH–H AND CH_2–H BONDS

—Dissociation energies, kcal./mole—		
E(CH—H)	E(CH_2—H)	References
92	86.4	76
78.4	79.5	83
87	83	123
84	92	136
129	78 ± 5	138

However, it may be noted here that the relative stability or instability of a particle far from proves that the ground state is a singlet or a triplet. Examples are known in which this is not true. For instance, the oxygen molecule, being in the triplet state, displays complete stability.

Based on the assumption that methylene is a non-linear molecule, the molecular orbitals method (77, 87, 88), led to a singlet structure for the ground state of methylene. The calculations were based only on qualitative considerations, carried out by a theoretical-group analysis. Careful consideration of these results revealed that the problem is much more complex, and only laborious calculations could establish the character of the ground state of methylene (78). It was suggested also that in the singlet state the H–C–H bond should have an angle of 120° while in the triplet state the molecule should be linear. On the other hand, calculations by the atomic orbitals method showed that the ground state of methylene was in the triplet state having a H–C–H angle of 140° (90). In this work, both the s^2p^2 and sp^3 configurations for the carbon atom were considered, taking the C–H bond length as 1.12 Å.

An opposite conclusion was reached from a study of the resonance of covalent and ionic structures. The result was a singlet methylene in the ground state with an angle of 140°. It was also concluded that a triplet state would correspond to an angle of 180° (72).

Moreover, while no attempt was made to determine whether methylene is a singlet or a triplet, but assuming that electrons of a covalent structure can occupy hybrid orbitals, the conclusion was reached that the H–C–H angle in the triplet state should be 109° 28′ (30).

Judging on pure chemical evidence, methylene is believed to be in the singlet state (122). Thus the addition of methylene to olefins is completely stereospecific, a fact which is in contrast with a biradical structure,
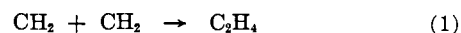
and which would bring structural changes in the olefins.

Although spectra are very informative for the determination of structures, unfortunately there are no spectral data available for methylene. The band system at λ4050 observed in the spectrum of comets (46, 47) and believed to belong to methylene, was proved to belong to a molecule with more than one carbon atom (28) and particularly to a molecule having three carbon atoms (17).

C. REACTIONS

One of the early evidences for the presence of methylene was its reaction with tellurium and selenium mirrors to produce telluroformaldehyde, $(CH_2Te)_n$, and selenoformaldehyde, $(CH_2Se)_n$, polymers (99, 102). The products thus formed when collected at different temperatures appear to have different physical properties (79). This is due to the different degree of polymerization of telluroformaldehyde and selenoformaldehyde. Methylene also reacts with mirrors of antimony and arsenic, but not with those of zinc, thallium, bismuth, cadmium, or lead (102).

The reactions of methylene with hydrogen depend on the temperature. Thus methylene formed in the decomposition of ketene, reacting with hydrogen below 200°, gives methane and butane (105). But at temperatures as high as 300° the main product is methane (8). A thermodynamic study of some of these reactions has been made (7), and these reactions were outlined

$$CH_2 + CH_2 \rightarrow C_2H_4 \quad (1)$$

$$CH_2 + H_2 \rightarrow CH_4 \quad (2)$$

$$CH_2 + H_2 \rightarrow CH_3 \quad (3)$$

$$CH_2 + CH_4 \rightarrow 2CH_3 \quad (4)$$

The first two reactions are strongly exothermic, requiring three-body collisions; reactions 3 and 4 are almost thermo-neutral and appear to require only small activation energies.

The production of methylene by the decomposition of diazomethane and its reactions with other compounds and especially with ethylenic bonds has received a great deal of attention (1, 27, 34, 35, 48, 103, 148). It was not until the observation that methylene reacts without discrimination with other molecules (27) that evidence was given that the methylene produced by the direct photolysis of diazomethane will account for a number of mixed reaction products (48, 122, 148). Thus photolysis of diazomethane in the presence of cis-2-butene or trans-2-butene in the liquid or gas phase does not isomerize the butene, but yields cis-2-dimethylcyclopropane and cis-2-pentene or trans-1,2-dimethylcyclopropane and trans-2-pentene (122). Failure to observe isomerization in the products cis- and trans-2-pentene from methylene and cis- and trans-2-butene, respectively, suggests that the intermediate in this

substitution reaction has structure II. Or when methylene reacts with cyclohexene, bicyclo[4.1.0]hep-

$$CH_3CH=CHCH_3 + CH_2 \rightarrow$$



$$CH_3CH=CH-C \rightarrow CH_3CH=CH-C$$

II
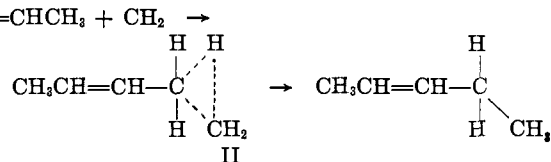
tane (norcarane) is not the only product, but small yields of the methylcyclohexenes also are obtained (69).
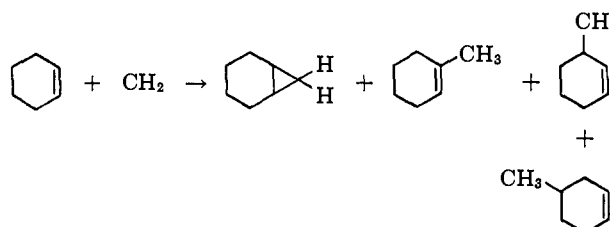

It has been shown (69) that a selective form of methylene can be formed in solution by sensitized photolysis or thermal catalytic decomposition. The sensitizer used is benzophenone and the catalysts are either copper powder or ferric dipivaloylmethide. Under these conditions the formation of by-products is excluded.

The expansion of aromatic rings in the presence of irradiated diazomethane to produce seven-membered rings involves methylene formation. Tropilidenes (III) form from sustituted phenyls by the addition of methylene (23, 24).

III, R=H,
(CH₃)₂CH,
C₆H₅, C₆H₁₁
(cyclohexyl)
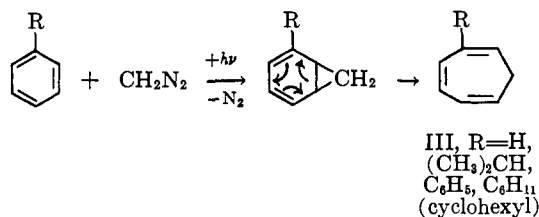
Ring expansion in the presence of methylene produced by the decomposition of diazomethane has been observed also with alicyclic compounds. Thus camphorquinone (IV) undergoes ring enlargement to the keto ether (V), hydrolyzed to homocamphorquinone (VI) (106).

$$CH_2N_2 \rightarrow CH_2 + N_2$$
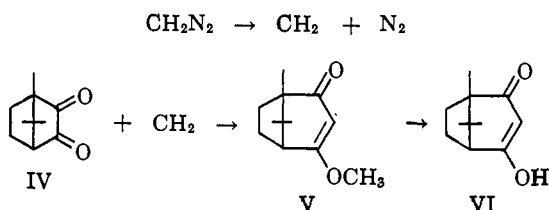
It is most probable that the formation of V takes place in two steps. In the first step one mole of methylene adds on the oxygen of one of the carbonyls of camphorquinone to form a carbonium ion, stabilized

through resonance (compare with section IVB). This carbonium ion undergoes rearrangement to produce the seven-membered ring.
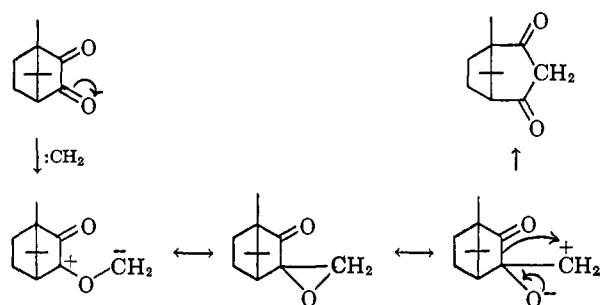

In the second step another mole of methylene adds, with the subsequent formation of V.
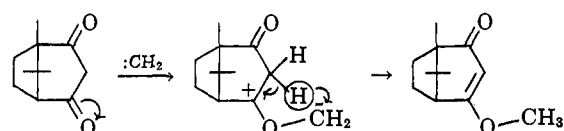
III. DIHALOCARBENES

A. DIFLUOROMETHYLENE

Difluoromethylene can be prepared by the photolysis of a number of fluorinated compounds (19, 134). In the photolysis of sym-tetrafluorodichloroacetone in the vapor phase, the main steps of the reaction have been verified (115) to be of the type

$$CF_2ClCOCF_2Cl + h\nu \rightarrow CF_2ClCOCF_2\cdot + Cl\cdot$$

$$CF_2ClCOCF_2\cdot \rightarrow CF_2Cl\cdot + CO + CF_2$$
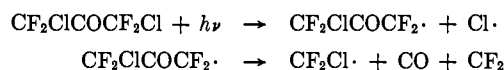
The absorption spectra have been detected as long as 20 msec. after the photolysis flash, and since no tetrafluoroethylene or volatile CF_2-telomers are formed, it appears that difluoromethylene is very unreactive. The half-life of difluoromethylene has been estimated from absorption spectra, and has been found to be of the order of one second (73).
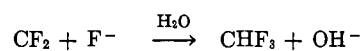
When dichlorodifluoromethane is excited in a discharge lamp, the ultraviolet spectrum shows the presence of difluoromethylene (65).

At high temperatures an equilibrium occurs between CF_2 and CF. Thus the absorption spectrum of tetrafluoromethane gas, thermally decomposed under equilibrium conditions in a graphite tube furnace, shows the bands of CF_2 at a temperature of 1900°K. and also the bands of CF at a temperature of 2400°K. (82).

Difluoromethylene can also be prepared by the decarboxylation of difluorochloroacetic acid (60)

$$ClCF_2COO^- \rightarrow [\overset{-\delta}{Cl}\ldots\overset{-\delta}{CF_2}\ldots\overset{-\delta}{COO^-}] \rightarrow Cl^- + CF_2 + CO_2$$
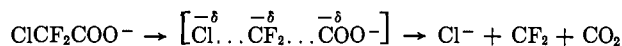
and was found to react readily with water, fluoride and chloride ions (54)

$$CF_2 + F^- \xrightarrow{H_2O} CHF_3 + OH^-$$

$$CF_2 + Cl^- \xrightarrow{H_2O} CHClF_2 + OH^-$$

$$CF_2 + H_2O \xrightarrow{H_2O} \begin{cases} \to CO + 2HF \\ \to HCOOH + 2HF \end{cases}$$
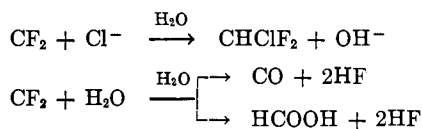
The fact that fluoride ions are more effective than chloride ions in combining with the intermediate difluoromethylene, as it is observed by comparing the relative yields of fluoroform and chlorodifluoromethane, it is not surprising even though their nucleophilicities are of the following order in other reactions (52): I > Br > Cl > F.

The fact is that the fluoride ions are poorer carbanion stabilizers than chlorides (58, 59), and thus the carbanion CF_3^- will react much faster than the carbanion CF_2Cl^-.

The ability of difluoromethylene to combine with nucleophilic reagents has been demonstrated with the use of molecules other than water or halogen ions. Difluoromethylene, being itself a strong electrophilic reagent (21, 118), would be expected to combine with nucleophilic reagents such as methanol, methoxide ions, or thiophenoxide ions. In fact, it has been found that difluoromethylene produced by the action of methanolic sodium methoxide on chlorodifluoromethane is more than one hundred times as effective in combining with thiophenoxide ions than in combining with methanol (56).

Difluoromethylene can also be formed by the reaction of potassium isopropoxide in isopropyl alcohol with chlorodifluoromethane (60).

$$(CH_3)_2CHO^- + CHClF_2 \rightleftarrows (CH_3)_2CHOH + CClF_2^-$$

$$CClF_2^- \to CF_2 + Cl^-$$
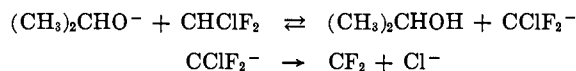
This reaction involves a concerted mechanism, as in the case of the hydroxide hydrolysis of fluorinated haloforms (55), with no formation of the carbanion $CClF_2^-$. It has been noticed that in the basic hydrolysis of haloforms the most reactive ones contain at least one fluorine atom and either a bromine or iodine atom is lost as an anion in the rate-controlling step of the reaction (58, 59). This shows that the fluorine atoms stabilize dihalomethylene formation better than other halogen atoms, speeding dihalomethylene formation and retarding the formation of the carbanion CX_3^-. Since the hydrolysis of chlorodifluoromethane and bromodifluoromethane is much faster than would be expected for carbanion formation (55), this alone shows that the carbanion CF_2X^- ($X = Cl$, Br) is not an intermediate in the production of difluoromethylene. This implies that a transition state is involved in the basic hydrolysis of these haloforms, with simultaneous removal of the haloform hydrogen and of the heterohalogen atom.

$$HO^- + HCF_2X \to [\overset{-\delta}{HO}...H...\overset{-\delta}{CF_2}...\overset{-\delta}{X}] \to HOH + CF_2 + X^-$$
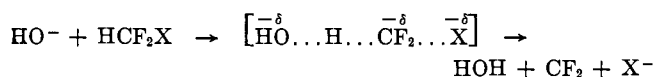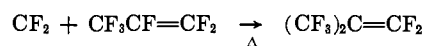
In addition to the other methods of preparation, difluoromethylene can also be formed by the pyrolysis of perfluorocyclobutane (2).

But as the temperature increases, difluoromethylene

$$\begin{matrix} CF_2-CF_2 \\ | \quad\quad | \\ CF_2-CF_2 \end{matrix} \xrightarrow{\Delta} CF_2 + CF_3CF=CF_2$$
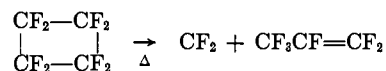
reacts with the perfluoropropylene to give perfluoroisobutylene exclusively (2).

$$CF_2 + CF_3CF=CF_2 \xrightarrow{\Delta} (CF_3)_2C=CF_2$$

In the same way, pyrolysis of difluorochloromethane produces difluoromethylene, which under optimum conditions dimerizes (12) to form tetrafluoroethylene, in a yield as high as 95% (98).

$$CHF_2Cl \xrightarrow{\Delta} CF_2 + HCl$$
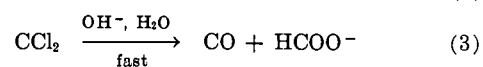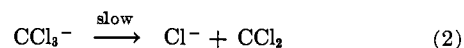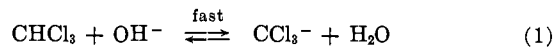
$$2CF_2 \to CF_2=CF_2$$
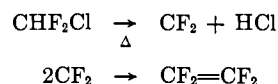
As far as the structure of difluoromethylene is concerned, it is still doubtful whether the ground state is in the singlet or triplet state. The calculations have been based mainly on spectral data. Thus the system of bands lying in the range of 2340–5000 Å., and obtained by the production of an electrical discharge in fluorocarbons, was shown to be due to difluoromethylene (134). Calculations based on a study of the bands in the range of 2400–3250 Å. revealed that difluoromethylene is in the ground state (73), having a non-linear structure (134), with a bond angle of 90–110° (29). These data point to a singlet state for difluoromethylene. However, it was pointed out (90), that the absorption and emission spectra of difluoromethylene are better explained by assuming a triplet state.

B. DICHLOROMETHYLENE

1. Preparation

The higher reactivity of chloroform than those of methylene chloride and carbon tetrachloride toward the potassium or sodium hydroxide hydrolysis could not be explained by considering the S_N1 and S_N2 mechanisms. In this basis, kinetic studies suggested the following mechanism for the basic hydrolysis of chloroform (50)

$$CHCl_3 + OH^- \underset{}{\overset{fast}{\rightleftharpoons}} CCl_3^- + H_2O \quad\quad (1)$$

$$CCl_3^- \xrightarrow{slow} Cl^- + CCl_2 \quad\quad (2)$$

$$CCl_2 \xrightarrow[fast]{OH^-, H_2O} CO + HCOO^- \quad\quad (3)$$

The intermediacy of dichloromethylene in chemical reactions has been suggested before (86, 89, 108, 130, 131, 132, 133). As far back as 1862 it was suggested (41) that chloroform was actually in the form $CCl_2 \cdot HCl$ and upon reaction with alkali it liberated the carbene.

The first equation of the basic hydrolysis of chloro-

form has been shown to hold, from the fact that chloroform undergoes a base-catalyzed deuterium exchange which is faster than its basic hydrolysis, showing that the carbon trichloride anion is formed rapidly (61). Also the hydrogen atom in chloroform is about as reactive as those in acetaldehyde or acetone (6), and it can be removed by a strong base. In the second step, it appears that an S_N1 mechanism operates and the negative trichloromethyl anion loses a chloride ion easier than it would a neutral molecule (50).

It is to be noted that dichloromethylene should have considerable resonance stabilization. However, the resulting energy gain is insufficient to provide dichloromethylene with complete stability such as in the other divalent carbon species, carbon monoxide or the isonitriles. The principal contributing structures for dichloromethylene would be
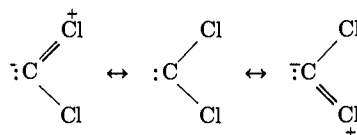
The dichloromethylene formed in the above hydrolysis, because of its electrophilic character (21, 118), combines with nucleophilic reagents such as water or halide ions (52)
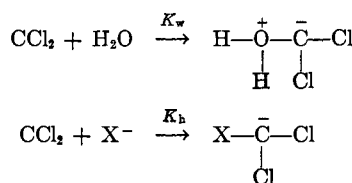

where K_w and K_h are the rate constants.

The ratio K_h/K_w has been termed the *competition factor* (52), and values for this ratio are a relative measure of the ability of these ions in combining with the carbene. A plot of the Swain equation (128)

$$\log (K_h/K_w) = SN_h$$

where S is a constant and N are nucleophilic constants, gives values which show that iodide ions are more effective in combining with the dichloromethylene than are bromide ions, which in turn are more reactive than chloride ions (52).

A modification in the above method of the preparation of dichloromethylene from chloroform was made by using potassium t-butoxide as the base in a solution of the alcohol (22) or in an inert solvent such as pentane (124).

$$CHCl_3 + (CH_3)_3CO^- \rightleftharpoons (CH_3)_3COH + CCl_3^-$$
$$CCl_3^- \rightleftharpoons CCl_2 + Cl^-$$
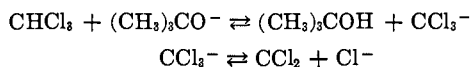
The superiority of t-butoxides over other alkoxides in this reaction may be related, at least in part, to decreased reactivity of the more highly hindered t-alcohol produced in the reaction with the carbene.

In addition to chloroform, other chlorohaloforms have been used as dichloromethylene precursors. It is known that in the formation of a carbene from a haloform an S_N1 ionization occurs first (50, 52). Thus when two different halogens are present, as in dichlorobromomethane (XII), three different carbenes (VIII, IX, X), are possible when equilibrium is attained. In non-polar solvents such as
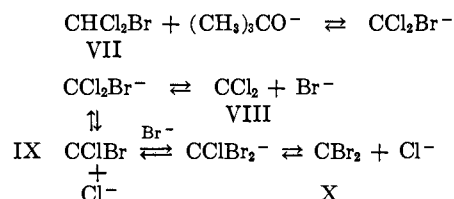

indene in which potassium halide is insoluble, only the carbenes VIII and IX are formed. This has been illustrated by the reaction of dichlorobromethane, indene, and potassium t-butoxide (97), which gives a mixture of 1,1-dichloro-1a,6a-dihydrocycloprop[a]indene (XI) and 1-chloro-1-bromo-1a,6a-dihydrocycloprop[a]-indene (XII). Of this
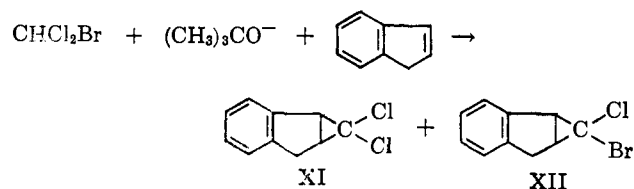
mixture 60% is XI showing that bromide ion is eliminated faster than chloride from the trihalomethyl anion of VII. Thus when dibromochloromethane (XIII) is used instead of dichlorobromomethane, the products of the reaction are a mixture of the *endo-* and *exo-*1-chloro-1-bromo-1a,6a-dihydrocycloprop[a]indenes (XIV) and not 1,1-dibromo-1a,6a-dihydrocycloprop-[a]indene (XV).
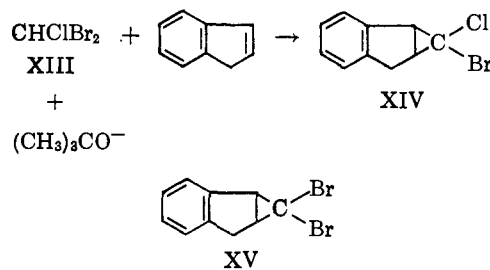
Although the formation of dichloromethylene by the action of alkyllithiums in ether solution on tetrahalomethanes (84) looks promising, the pertaining literature

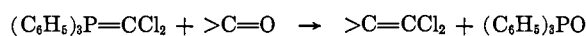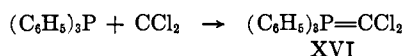$$CCl_3X + RLi \rightarrow CCl_3Li + RX$$
$$CCl_3Li \rightarrow CCl_2 + LiCl$$
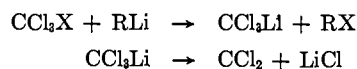
is very poor. The efficiency of the method is seen in Table II, which lists the yields of dichloronorcarane obtained by the addition of dichloromethylene to cyclohexene.

TABLE II

YIELDS OF DICHLORONORCARANE OBTAINED IN THE REACTION OF
CYCLOHEXENE WITH TETRAHALOMETHANES AND ALKYLLITHIUMS

Reactants		
Tetrahalomethane	Alkyllithium	Yield, %
CCl₄	CH₃Li	8
CCl₄	n-CH₃(CH₂)₃Li	50
CCl₃Br	CH₃Li	67
CCl₃Br	n-CH₃(CH₂)₃Li	91
CCl₃I	CH₃Li	71

However, the reaction of alkyllithiums with chloroform appears to be more important, since the product dichloromethylene can be trapped by the nucleophilic (70) triphenylphosphine to form the ylide, triphenylphosphinedichloromethylene* (XVI) (113). This reaction takes place also when potassium *t*-butoxide is used instead of the alkyllithium (124). In both cases, the reagent triphenylphosphinedichloromethylene can undergo the Wittig reaction, and thus provides a general method of synthesizing substituted vinyl chlorides. Treatment of solutions of triphenylphosphinedichloromethylene with ketones or aldehydes gives the expected vinyl chloride.

$$(C_6H_5)_3P + CCl_2 \rightarrow (C_6H_5)_3P{=}CCl_2$$
XVI

$$(C_6H_5)_3P{=}CCl_2 + {>}C{=}O \rightarrow {>}C{=}CCl_2 + (C_6H_5)_3PO$$

Recently, a new method of dichlorocarbene formation has been developed. It involves the reaction of chloroesters of acetic acid with alkoxides in a solution of an inert solvent.

$$CCl_3COR + RO^- \rightarrow CCl_3\overset{O^-}{\underset{OR}{C}}OR \rightarrow CCl_2 + Cl^- + ROCOR$$
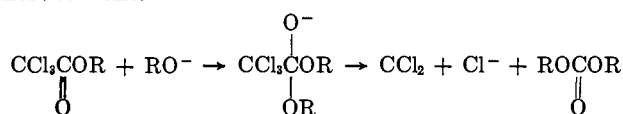
Although a yield of 10% of 1,1-dichloro-2,2-dimethylcyclopropane was obtained from the reaction of *t*-butyl dichloroacetate with potassium *t*-butoxide and isobutylene (93), ethyl trichloroacetate has been used more successfully with potassium *t*-butoxide, sodium ethoxide and sodium methoxide (96). The yields of cyclopropanes produced in the last reaction range from 72 to 88%. This reaction affords significantly higher yields of cyclopropanes than analogous reactions in which chloroform is used as the carbene precursor. Another advantage of this method is that sodium methoxide can be purchased commercially. A comparison of the yields of cyclopropanes obtained by the two methods is made in Table III.

If the sodium salt of trichloroacetic acid is used instead of the ester, the carbene is produced by the more thermal decomposition of the salt in an inert solvent (136a).

$$CCl_3COONa \xrightarrow{\Delta} CCl_2 + NaCl + CO_2$$
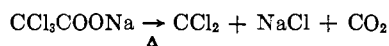
* When diazomethane is used as the carbene source, then the stable compound (C₆H₅)₃P=N–N=CH₂ is obtained instead of the expected triphenylphosphinemethylene. This unsuccessful attempt is considered due to the unstability of triphenylphosphinemethylene.
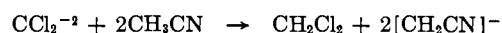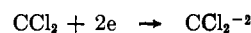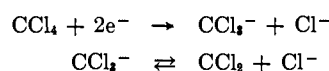
TABLE III

COMPARISON OF THE % YIELDS OF CYCLOPROPANES OBTAINED
FROM OLEFINS BY THE ETHYLTRICHLOROACETATE AND
CHLOROFORM METHODS

| Base	CCl₃COOC₂H₅ᵃ		CHCl₃	
	1,1-Dichloro-2,2-dimethyl-cyclo-propane	7,7-Dichloro-norcar-ane	1,1-Dichloro-2,2-dimethyl-cyclo-propane	7,7-Dichloro-norcar-ane
Potassium *t*-butoxide	86	72	65ᵇ	59ᵇ
Sodium ethoxide	82	—	—	—
Sodium methoxide	76	88	—	38ᶜ

ᵃ Ref. 96. ᵇ Ref. 22. ᶜ Ref. 145.

The polarographic methods which have been found to be useful in proving the existence of stable free radicals, were used also in identifying dichloromethylene as a reaction intermediate, in the electrolytic reduction of carbon tetrachloride in acetonitrile solution (139). The following reactions were found to occur

$$CCl_4 + 2e^- \rightarrow CCl_3^- + Cl^-$$
$$CCl_3^- \rightleftarrows CCl_2 + Cl^-$$
$$CCl_2 + 2e \rightarrow CCl_2^{-2}$$
$$CCl_2^{-2} + 2CH_3CN \rightarrow CH_2Cl_2 + 2[CH_2CN]^-$$

Additional proof of the formation of dichloromethylene in the above electrolysis was obtained by electrolyzing carbon tetrachloride at −20° in the presence of 2,3-dimethyl-2-butene. Dichloromethylene was thus trapped to give 1,1-dichloro-2,2,3,3-tetramethylcyclopropane (139).

$$CCl_4 + 2e \rightarrow CCl_3^- + Cl^-$$
$$CCl_3^- \rightleftarrows CCl_2 + Cl^-$$
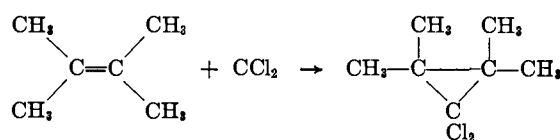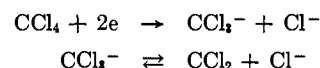
In all the cases of dichloromethylene formation discussed so far, the preparation took place in polar or non-polar solvents and at low temperatures. In any case, the dichloromethylene formation may be assumed in the pyrolysis of chloroform at 450–525°. The main products are tetrachloroethylene and hydrogen chloride (111).

$$2CHCl_3 \xrightarrow{\Delta} CCl_2{=}CCl_2 + 2HCl$$
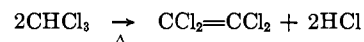
The formation of tetrachloroethylene was studied kinetically, and it was found that the pyrolysis can be best described as (112)

$$CHCl_3 \rightarrow \cdot CHCl_2 + Cl\cdot$$
$$CHCl_3 + Cl\cdot \rightarrow HCl + \cdot CCl_3$$
$$\cdot CCl_3 \rightarrow CCl_2 + Cl\cdot$$
$$CHCl_3 + CCl_2 \rightarrow CCl_2{=}CCl_2 + HCl$$
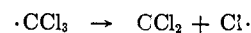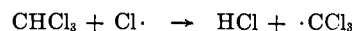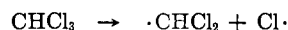
The assumption that a C–Cl bond is broken first and not the C–H bond is supported by the negligible isotope effect observed in comparing the rates of decomposition of $CHCl_3$ and $CDCl_3$ and shows only a 2% difference.

The intermediacy of dichloromethylene in the pyrolysis of chloroform has received further support from the fact that carbon monoxide is produced in the presence of water, and phosgene in the presence of oxygen (80).

2. Addition to Olefins
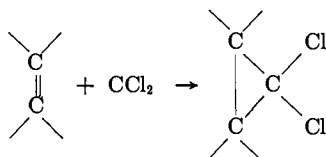
In the methods of preparation of dichloromethylene, it became obvious that one of the most characteristic reactions of dichloromethylene is its addition to olefins with the formation of cyclopropane derivatives.

However, the generality of this reaction has not been proved in all cases. For instance, while β-pinene affords the expected cyclopropane, α-pinene leads to unstable, unsaturated products (22).

The only other known reactions in which a species with a vacant orbital adds to olefins is the formation of the bromonium ion in bromination reactions and the addition of oxygen in epoxidation reactions.
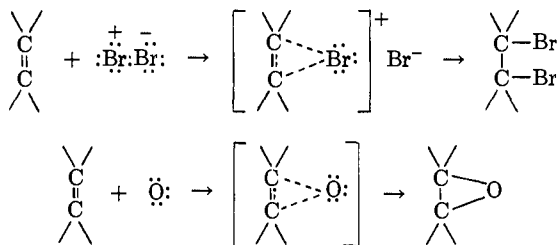
The addition of dichloromethylene to olefinic double bonds depends on the degree of nucleophilicity of the individual olefin (21). This nucleophilicity of olefins fully accounts for the inertness of dichloromethylene toward hexachloro-1,3-butadiene in which the large number of electronegative substituents produces a depletion of the π-bonds (146, 147).

The rate of addition of dichloromethylene to cyclohexene has been chosen as a standard to which the other olefins are referred. Table IV illustrates the relative reactivities of some olefins toward dichlorocarbene, the over-all difference being quite large, 2,3-dimethyl-2-butene reacting about 400 times faster than 1-pentene (21).

It will be noted that the reactivity of dichloromethylene toward the olefins increases with the degree of alkyl substitution in the order: tetrasubstituted olefin > trisubstituted > unsym-disubstituted > sym-di-

TABLE IV
REACTIVITY OF OLEFINS TOWARD DICHLOROMETHYLENE

| Olefin	K_1(olefin)/K_2(cyclohexene)
2,3-Dimethyl-2-butene	53.6
2-Methyl-2-butene	23.4
Isobutylene	8.3
2-Methyl-1-butene	5.5
trans-2-Pentene	2.1
Ethyl vinyl ether	1.8
cis-2-Pentene	1.6
1-Hexene	0.18
1-Pentene	0.13

substituted > monosubstituted. This series is in complete agreement with the relative reactivities of olefins in bromination and epoxidation, which attests to the similarity of the mechanism of these reactions.

It has been suggested (21) that the transition state of the addition of dichloromethylene to olefin is a resonance hybrid, with main contributing structures such as)
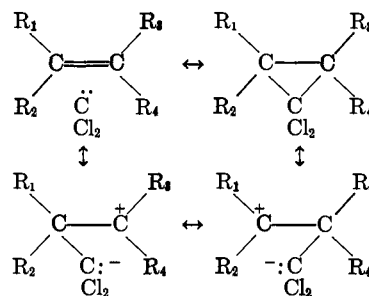
The structures bearing the positive charge on the tertiary carbon atom must be the ones contributing most in the case of tetraalkyl olefins, since tertiary carbonium ions are more stable than secondary or primary.

The formation of cyclopropanes from olefins and dichloromethylene is one of the most conclusive evidences for the intermediacy of dichlorocarbene. The alternative mechanism for the formation of cyclopropanes, in which the trichloromethyl anion adds to olefins to form a carbanion from which the cyclopropanes form by displacement of chloride ion, is not very likely, because it is well known that olefins with an unactivated double bond do not tend to add anions. Furthermore, it never has been possible to isolate from these reactions the saturated trihalomethyl derivative
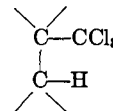
which should form from the carbanion upon addition of a proton.

3. Ring Expansions

The use of dichloromethylene makes it possible to synthesize not only cyclopropanes but also a variety of other compounds by the ring expansion of certain aromatic and heterocyclic systems. It was suggested that the well-known reactions of pyrrole and indole with chloroform and base to form 3-chloropyridine and
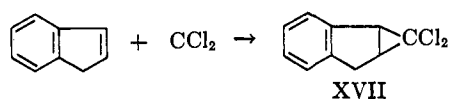
3-chloroquinoline, respectively, involve the addition of dichloromethylene (94).
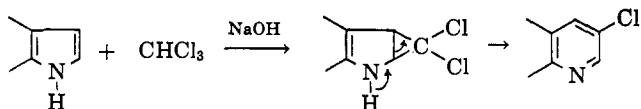
Using a similar type of reaction, indene is successfully converted to 2-chloronaphthalene.* The carbene is generated from chloroform and indenylsodium or chloroform and potassium t-butoxide. When potassium t-butoxide is used as the base (95), the yield of 2-chloronaphthalene is as high as 65%, while with indenylsodium (94), only a 10% yield is obtained.

The initial step in these reactions is the formation of 1,1-dichloro-1a,6a-dihydrocycloprop[a]indene (XVII), which can be isolated in yields of 65–70%. Dehydrohalogenation of XVII with alcoholic potassium hydroxide gives the chloronaphthalene.
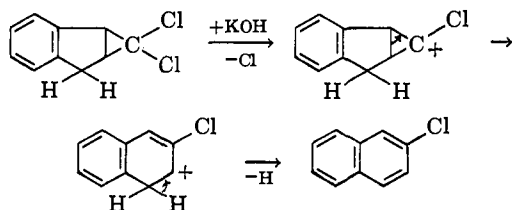
Of an exactly similar nature is the expansion of the isomeric mixture of XIV to give a 1:1 mixture of 2-chloro(XVIII) and 2-bromonaphthalene (XIX) (97).
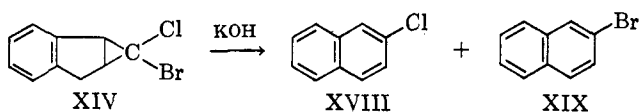
A by-product in the reaction of dichloromethylene and indene is an azulene, which forms in a very small yield by the expansion of the benzene ring of indene (94, 95). This shows that aromatic double bonds are less reactive than olefinic double bonds. However, if an electron-donating group is present on an aromatic ring, cyclopropyl adducts are formed which undergo ring expansion to produce chlorotropones. The reaction has been used with 1- and 2-methoxynaphthalene and with 9-methoxyphenanthrene (94a). The carbene was generated from ethyl trichloroacetate and sodium meth-

oxide. Hydrolysis of the chlorotropone converts it to tropolone, and thus provides a method for the synthesis of tropolones.

The generation of dichloromethylene by the ethyl trichloroacetate method has been used also for the ring expansion of some heterocyclic compounds. Thus when ethyl trichloroacetate is added to a mixture of dihydropyran (XX) and sodium methoxide in pentane, 2-oxa-7,7-dichloronorcarane (XXI) is obtained (110).

$$CCl_3CCOC_2H_5 + CH_3O^- \rightarrow CCl_2$$
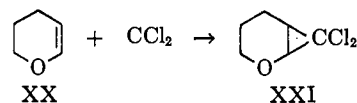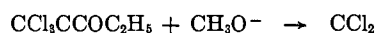
Compound XXI is readily converted to 2,3-dihydro-6-chlorooxepine (XXII) by heating at 140–150° a mixture of XXI and quinoline under reduced pressure (110).
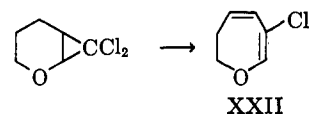
This reaction is analogous to the conversion of dichloronorcarane into cycloheptatriene (XXIII) (145).

$$CHCl_3 + CH_3O^- \rightarrow CCl_2$$
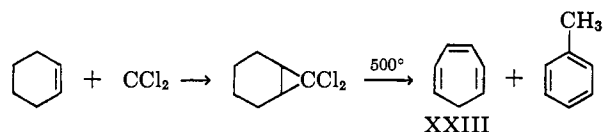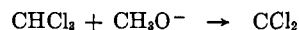
The mechanism of the decomposition of XXI into XXII involves an allylic carbonium ion (XXIX), which loses a proton and is thus transformed into XXII.
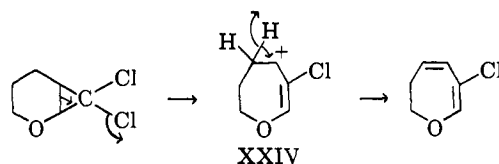
Extension of the method to 2H-1-benzothiopyran (XXV) and 4H-1-benzothiopyran (XXVI) did not produce ring expansion. Instead, insertion products were obtained with XXV, and 2-chloronaphthalene with XXVI.

Thus when dichloromethylene, generated from ethyl trichloroacetate and sodium methoxide, is allowed to react with 2H-1-benzothiopyran at room temperature, a 2:1 mixture of 2-dichloromethyl-2H-1-benzothiopyran (XXVII) and 4-dichloromethyl-4H-1-benzothiopyran (XXVIII) are formed (92).

---

* Attempts to convert cyclopentadiene into chlorobenzene by this method were unsuccessful. The products obtained appear to be the dimer of cyclopentadiene and also higher polymers.

NOTE ADDED IN PROOF.—However, it has been claimed that dichloromethylene does indeed add to cyclopentadiene, as well to cycloheptatriene, under these conditions, forming chlorobenzene and 1-chlorobenzocyclobutene, respectively; see A. P. ter Borg and A. F. Bickel, *Proc. Chem. Soc.*, 283 (1958).

$$CCl_3COOC_2H_5 + CH_3O^- \rightarrow CCl_2$$

XXV   XXVII   XXVIII

The initial step of this reaction is the addition of the electrophilic dichloromethylene to the nucleophilic sulfur to form the intermediate XXIX, which then re-

XXIX
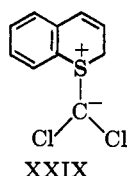
arranges to XXVII and XXVIII.

An analogous insertion reaction of dichloromethylene has been observed in the presence of certain enamines, where a dichloromethyl group is introduced rather than the formation of the expected cyclopropane (126). Also in the Reimer–Tiemann reaction, where dichloromethylene is the reactive species and not chloroform, an acetal, if formed at all, does not appear to be the main path by which the aldehyde is formed, but rather the insertion product o-dichloromethylphenolate (135, 149) is formed.

However, insertion products are not formed when 4H-1-benzothiopyran (XXVI) reacts with dichloromethylene, but the cyclopropyl adduct 1,1-dichlorocycloprop[b][1]benzothiopyran (XXX) is obtained (92). Attempts to convert XXX into chlorothiepin (XXXI)

XXX   XXXI

by heating in quinoline resulted in a 27% yield of 2-chloronaphthalene and elementary sulfur.

C. DIBROMOMETHYLENE

1. Preparation

Dibromomethylene (XXXII) forms as an intermediate in the alkaline hydrolysis (60, 107, 121) of bromoform, or under anhydrous conditions using an alkali metal alkoxide in a solution of the alcohol (22, 60, 117).

$$CHBr_3 + :B \rightleftarrows CBr_3^- + HB$$
$$CBr_3^- \rightleftarrows CBr_2 + Br^-$$
XXXII
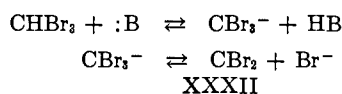
Other strong bases such as methyllithium and n-butyllithium have been used also to effect dibromomethylene formation by their action on dibromomethane (15) and tetrabromomethane (84), respectively. However,

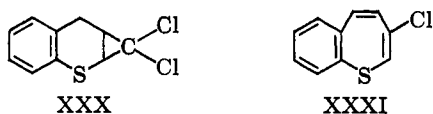while negligible yields of dibromocyclopropanes were obtained from n-butyllithium and tetrabromomethane in the presence of olefins, it was not possible to demonstrate the formation of dibromomethylene in the reaction of methyllithium and dibromomethane.

From a study of the addition of dibromomethylene to olefins, it has been suggested that dibromomethylene is a planar molecule having sp² hybridization and a vacant p-orbital. In the ground state (XXXIII) an unshared electron pair may overlap with this vacant orbital (117, 122).

XXXIII
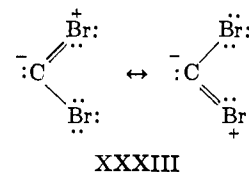
2. Addition to Olefins

Dibromomethylene in the presence of olefins reacts readily to form 1,1-dibromocyclopropanes (22).
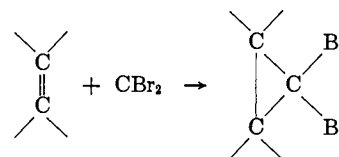
The addition of dibromomethylene to olefins is stereospecific, bringing no structural changes in the latter (117, 122). Thus reaction with the cis- or trans-2-butene gives, respectively, cis- (XXXIV) or trans-1,1-dibromo-2,3-dimethylcyclopropane (XXXV).

XXXIV

XXXV
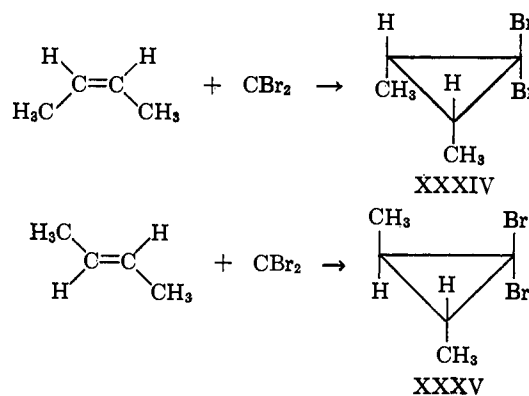
The rate of addition of dibromomethylene to olefins depends greatly on the alkyl substituents of the olefin (118) and it is of the same order as in the case of dichloromethylene (21). However, dibromomethylene reacts slower than dichloromethylene. In Table V a comparison of the reaction rates of dibromo- and dichloromethylene with substituted olefins is made with the rate of addition to cyclohexene chosen as a standard.

The intermediate of the addition of dibromomethyl-

Table V

REACTIVITY OF DIBROMO- AND DICHLOROMETHYLENE WITH OLEFINS

Olefin	K_1(olefin)/K_2(cyclohexene)	
	CBr$_2$[a]	CCl$_2$[b]
2,3-Dimethyl-2-butene	8.7	53.6
2-Methyl-2-butene	8.0	23.4
Anethol	3.0	—
Isobutylene	2.5	8.3
Styrene	1.0	—
1-Hexene	0.17	0.18

[a] Ref. 118. [b] Ref. 21.

ene to olefins has structure XXXVI rather than that of the diradical XXXVII (117, 118, 122).

XXXVII   XXXVI

The formation of the diradical XXXVII would involve a reversible or irreversible association of the carbene with the olefin.
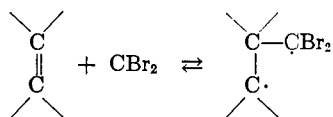
A reversible mechanism for the formation of the diradical is ruled out by the failure to isolate isomers of the recovered olefins produced by rotation around the $>$C–C$<$ bond. If an irreversible process takes place, then an equilibration mixture of isomeric cyclopropanes would be obtained, contrary to the complete stereospecificity of the reactions. These phenomena could imply that the life of the diradical XXXVII does not exceed 10^{-10} sec., the time required for rotation around the single bond. However, this point has not been clarified as yet.

Structure XXXVI has received more support in view of the fact that the addition of dibromomethylene to the 2-butenes is exclusively *cis*. Mechanistically the *cis* addition supports a direct addition of the carbene to the olefin, disfavoring the formation of the diradical (25).
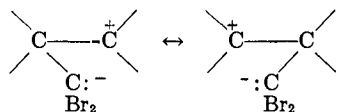
The partially formed cyclopropane XXXVI may be better represented as a resonance hybrid with some carbonium ion character.

The contribution to the hybrid of the structures bearing positive charge must be responsible for the greater reactivity of polysubstituted olefins toward dibromomethylene, since tertiary carbonium ions are more stable than secondary and primary ions (118).

The formation of dibromocyclopropanes from olefins and dibromomethylene can be regarded as the first stage of a method for the synthesis of allenes. The allenes are prepared in good yields on treating the 1,1-dibromocyclopropanes with finely dispersed sodium deposited on alumina, or with magnesium in dry ether (26). The mechanism of this unusual reaction most probably involves the formation of another carbene which then forms the allene.
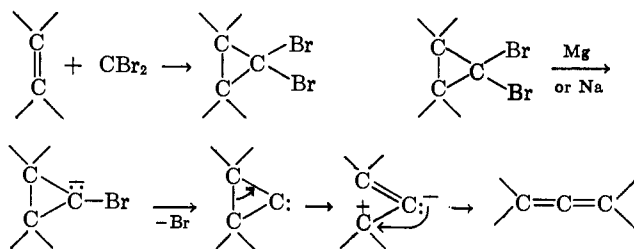
This reaction not only provides a synthetic route to allenes, but it also represents a new method of extending a carbon chain by one carbon atom.

If instead of magnesium or sodium, aqueous alcoholic silver nitrate is used with the dibromocyclopropanes, then halogen-substituted allylic alcohols are obtained (120).
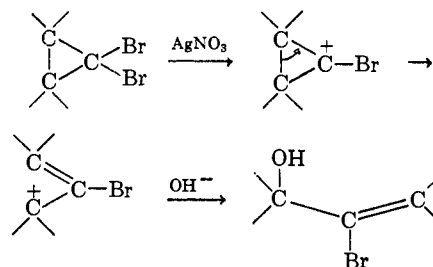
3. Ring Expansions

In an analogous way to the addition of dichloromethylene to indene, dibromomethylene adds to substituted indenes to form bromonaphthalenes (95).

The molecule of substituted indenes in the 1-position under alkaline conditions exists as a tautomeric equilibrium (104).
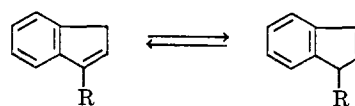
Apparently, one would expect, since the 1,2-positions are sterically hindered, that the main product of the reaction of dibromomethylene with methylindene would be 1-methyl-3-bromonaphthalene (XXXVIII).

However, it is interesting that 1-methyl-2-bromonaphthalene (XXXIX) is obtained exclusively in 44% yield (95).
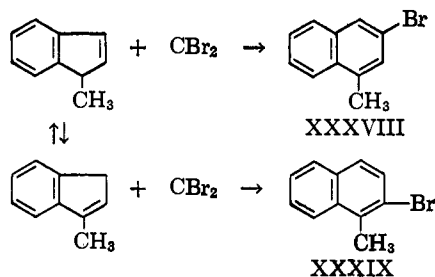
Of a similar nature, although under different conditions, is the conversion of 2,2-dibromobicyclo[3.1.0]-hexane into a halogen-substituted allylic alcohol (120).
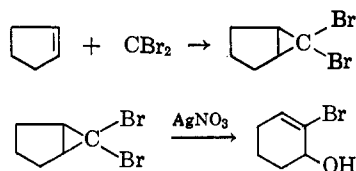
D. DIIODOMETHYLENE

By the action of sodium ethoxide on iodoform, diiodomethylene is formed (60).

$$CHI_3 + C_2H_5O^- \rightleftharpoons CI_3^- + C_2H_5OH$$
$$CI_3^- \rightleftharpoons CI_2 + I^-$$
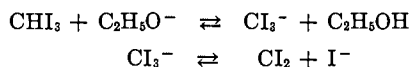
Subsequently, the diiodomethylene undergoes reactions with the excess ethoxide ions to give acetaldehyde and methylene iodide (60).

$$CI_2 + C_2H_5O^- \rightarrow CH_3CHO + CHI_2^-$$
$$CHI_2^- + C_2H_5OH \rightarrow CH_2I_2 + C_2H_5O^-$$
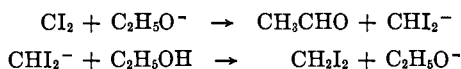
The typical reaction of dihalocarbenes in adding to ethylenic double bonds is also followed by diiodomethylene. The diiodomethylene formed by the method of potassium t-butoxide and iodoform adds to cyclohexene to give diiodonorcarane (XL) (22).

$$CHI_3 + (CH_3)_3CO^- \rightleftharpoons CI_3^- \rightleftharpoons CI_2 + I^-$$
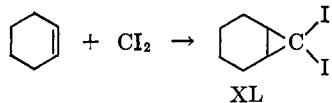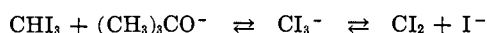
Although dichloromethylene and dibromomethylene add to indenes to form chloro- and bromonaphthalenes, it has not been possible to demonstrate the formation of iodonaphthalene by the reaction of iodoform with potassium t-butoxide and indene (95). Instead, methylene iodide is formed in a 46% yield.

E. CHLOROFLUOROMETHYLENE

When dichlorofluoroacetic acid is decomposed thermally in an aqueous solution at 70–100°, the intermediate chlorofluoromethylene, CClF, forms

$$Cl_2CFCOO^- \rightarrow Cl_2CF^- + CO_2$$
$$Cl_2CF^- \rightarrow CClF + Cl^-$$
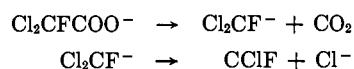
which undergoes rapid hydrolysis to give a number of products (53)

$$CClF \xrightarrow{H_2O} HCl, HF, CO, \text{ and } HCOOH$$
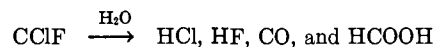
Chlorofluoromethylene has also been prepared by the basic hydrolysis of dichlorofluoromethane (51).

$$CHCl_2F + OH^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CCl_2F^- + H_2O$$
$$CCl_2F^- \overset{k_3}{\rightarrow} CClF + Cl^-$$
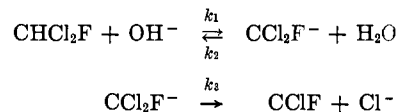
The approximate kinetic equation for this hydrolysis has been found (51) to be

$$-d[CHCl_2F]/dt = [k_1k_3/(k_2 + k_3)][CHCl_2F][OH^-]$$

This equation gives rate values which show that dichlorofluoromethane reacts with alkali much faster than methylene chloride. The explanation for this fact is evidently that the hydrolysis of dichlorofluoromethane does not involve a bimolecular nucleophilic substitution (SN2), but the reaction begins with a rapid and reversible formation of the anion CCl_2F^-, which then loses a chlorine atom (51). A chloride anion is lost rather than a fluoride, in view of the fact that fluorine atoms stabilize carbene formation better than the other halogens (58, 59).

Chlorofluoromethylene, prepared from dichlorofluoromethane and potassium t-butoxide, in the presence of cyclohexene undergoes reaction to give a mixture of $endo$- (XLI) and exo-chlorofluoronorcarane (XLII) (97).

$$CHCl_2F + (CH_3)_3CO^- \rightleftharpoons CCl_2F^- + (CH_3)_3COH$$
$$CCl_2F^- \rightarrow CClF + Cl^-$$
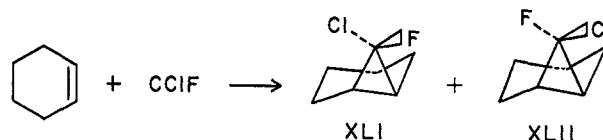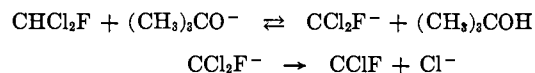
If indene is used instead of cyclohexene, 1-chloro-1-fluoro-1a,6a-dihydrocycloprop[a]indene (XVIII) is obtained initially, which on prolonged heating in ethanol gives a 9% yield of 2-fluoronaphthalene (XLIV) (97).
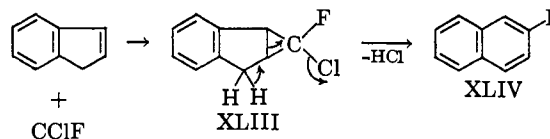
IV. CARBENES OTHER THAN DIHALOMETHYLENES

A. ALKOXYHALOMETHYLENES

Evidence has been given that isopropoxyfluoromethylene (XLV) forms during the basic decomposition of chlorodifluoromethane with potassium isopropoxide, in dry isopropyl alcohol (57). The mechanism of this re-

action has been formulated (60) to involve difluoromethylene as intermediate which then reacts with the isopropyl alcohol to form the isopropoxyfluoromethylene.

$$CHClF_2 + (CH_3)_2CHO^- \rightleftarrows CClF_2^- + (CH_3)_2CHOH$$

$$CClF_2^- \rightarrow CF_2 + Cl^-$$

$$(CH_3)_2CHOH + CF_2 \rightarrow (CH_3)_2CH\overset{+}{O}-\overset{-}{C}F_2 \underset{H}{|} \xrightarrow[-HF]{}$$

XLV

Similarly, dichlorofluoromethane reacts with dilute potassium isopropoxide to form also isopropoxyfluoromethylene via the chlorofluorocarbene (60) instead via difluoromethylene.

The isolation of triisopropyl orthoformate as the sole product (71% yield) from the above reaction is rather surprising. Chloroform and bromoform under the same conditions yield carbon monoxide, propylene, and isopropyl ether in addition to the orthoformate. The behavior of dichlorofluoromethane seems clearly attributable to the ability of isopropoxyfluoromethylene to retain the fluorine atom. On the other hand, the isopropoxyhalomethylene produced from either chloroform or bromoform loses a halide ion to give the cation $(CH_3)_2CHOC^+$, which then undergoes reactions to form the products isolated.
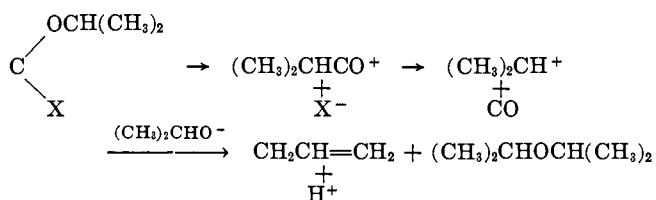
When chlorodifluoromethane reacts with sodium methoxide in dry methyl alcohol to produce methyl orthoformate, the intermediate carbene methoxyfluoromethylene (XLVI) is formed (56).

$$CHClF_2 + CH_3O^- \rightarrow CF_2 + CH_3OH + Cl^-$$

$$CH_3OH + CF_2 \rightarrow CH_3\overset{+}{O}-\overset{-}{C}F_2 \underset{H}{|} \xrightarrow[-HF]{}$$

XLVI
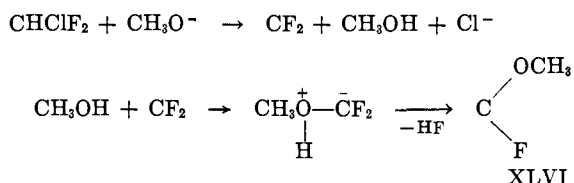
It is noticeable that this last reaction is initiated by an α-elimination, and proceeds by a mechanism not involving a trihalomethyl carbanion (55).

B. CARBETHOXYMETHYLENE

An analogous reaction to the photolysis of diazomethane is the photochemical decomposition of ethyl diazoacetate (22) to produce carbethoxymethylene (XLVII).
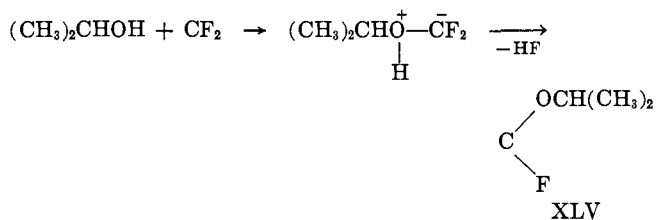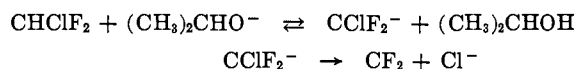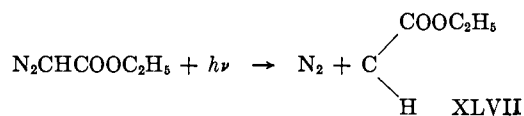

Carbethoxymethylene adds to the cis- or trans-2-butene stereospecifically, a reaction which has been used to detect this carbene as a reaction intermediate (122). The rate of addition to olefins was found to be much slower than that of the dihalocarbenes, but it is of the same order (116).

The mechanism of the addition of carbethoxymethylene to aromatic systems (10) to form expanded rings resembles the one of the addition of methylene to substituted benzene rings to form tropilidines. This method is a route to the synthesis of tropolones by the ring expansion of methoxylated benzenes (63). The oxygen atoms of the tropolone ring are thus provided initially, and the intermediate cycloheptatriene (XLVIII) is simultaneously hydrolyzed and dehydrogenated to the tropolone by bromine.
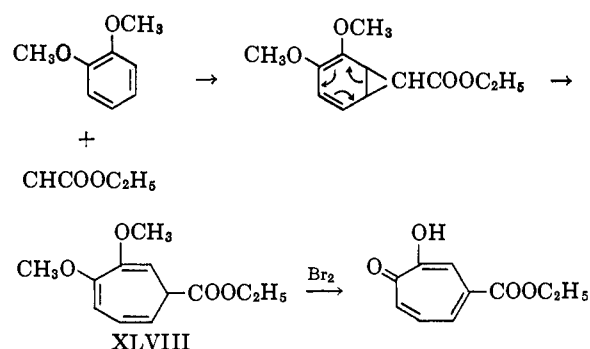
In the same way stipitatic acid (XLIX) has been synthesized from 1,2,4-trimethoxybenzene.
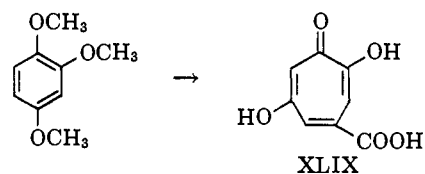
However, certain aromatic systems show some peculiarities. For instance, in the presence of anthracene, one should expect that carbethoxymethylene would add to the most reactive centers of anthracene, namely, the 9- and 10-positions. Instead, carbethoxymethylene adds across the 1,2-position, reacting as an alkene double bond forming a cyclopropane derivative (3).

In the presence of phenylbutadiene the addition takes place at the terminal position (137) because a concerted

electrophilic attack of carbethoxymethylene to the terminal double bond allows delocalization of the positive charge formed in the transition state through the conjugated styryl residue.

L

After the initial electrophilic addition, the species L has a nucleophilic center in the form of a non-bonded pair of electrons on the methylene carbon. Nucleophilic attack of these electrons, couple with the resulting localization of the electrons of the original double bond to form the remaining bonds of the cyclopropane ring.

The addition of carbethoxymethylene to the terminal position of conjugated systems is not surprising in view of the fact that the dihalocarbenes yield 1,2-addition products with butadiene (146, 147)

$$CH_2{=}CHCH{=}CH_2 + CX_2 \rightarrow CH_2{-}CHCH{=}CH_2$$
$$\diagdown C \diagup$$
$$X_2$$

In the presence of ketones, carbethoxymethylene adds on the oxygen of the carbonyl group to form an ether (42, 66).

$$R_1{-}CH{=}C{-}O{-}CH_2COOC_2H_5$$
$$|$$
$$R_2$$

When a more basic atom than the oxygen of the carbonyl group is present in the ketone, then the product is not only an ether. For instance, the reaction of carbethoxymethylene with 2-pyridone is not exclusively

but carbethoxymethylene adds also on the nitrogen to give N-substituted pyridones (81).

It is still possible to assume the intermediate formation of carbethoxymethylene in a number of reactions. The carbene is formed generally by the thermal de-

composition of ethyl diazoacetate. Thus on heating ethyl diazoacetate with water, alcohols or halogens, nitrogen is eliminated and substitution takes place.

It is also suggested that in the long-known reactions of ethyl diazoacetate with thiophene and diethyl azocarboxylate, to form ethyl cyclopropanodihydrothiophene-5-carboxylate and triethyl hydrazimethanecarboxylate, respectively

$$N_2CHCOOC_2H_5 \xrightarrow[\Delta]{} :CHCOOC_2H_5 + N_2$$

carbethoxymethylene is the reactive species and not ethyl diazoacetate.

C. DIPHENYLMETHYLENE

In attempts to produce the diphenylmethyl free radical by pyrolysis of benzhydryl bromide (LI) no radical could be detected (43). The pyrolysis proceeds exclusively to the formation of fluorene and hydrogen bromide. The mechanism of the preparation of fluorene seems to take place through formation of diphenylmethylene (LII) and subsequent hydrogen migration.

Diphenylmethylene has been prepared also by the diazo method. Photolysis of diphenyldiazomethane (LIII) at low temperatures produces LII (20).

$$(C_6H_5)_2CN_2 + h\nu \rightarrow C_6H_5{-}C{-}C_6H_5 + N_2$$
$$\text{LIII} \qquad\qquad \text{LII}$$

Diphenylmethylene reacts readily with diphenyldiazomethane to give benzophenone azine (LIV), and with oxygen to form benzophenone (LV) (20).

$$(C_6H_5)_2C=N-N=C(C_6H_5)_2 \qquad C_6H_5-\underset{\underset{O}{\|}}{C}-C_6H_5$$

$$\text{LIV} \qquad\qquad \text{LV}$$

When diphenylmethylene is prepared by the thermal decomposition of diphenyldiazomethane (91), the nature of the products of the reactions of diphenylmethylene depends directly on the solvent used. When decomposition takes place without solvent or in benzene solution, benzophenone azine (LIV) is obtained exclusively. If petroleum ether is used, benzophenone azine, sym-tetraphenylethane, and a molecular complex of this substance with benzophenone azine are formed. It was suggested that the formation of sym-tetraphenylethane takes place by the reaction of diphenylmethylene with the solvent petroleum ether to form diphenylmethyl radicals, which then dimerize to give the substituted ethane.

Rather stable substituted diphenylcarbenes (LVI) have been prepared by the pyrolytic and photolytic decomposition of the corresponding diazo compounds (LVII) (152).

LVIa, LVIIa; R₁, R₂, R₃ = CH₃
LVIb, LVIIb; R₁, R₂, R₃ = Cl
LVIc, LVIIc; R₁ = CH₃; R₂, R₃ = OCH₃
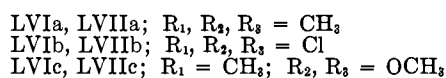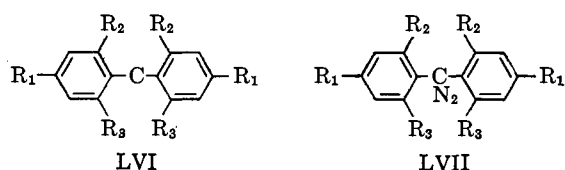
The inability of the species LVI to react readily, a behavior characteristic of divalent carbon, is the result of steric hindrance exerted by the groups R₂ and R₃, which thus render stable these carbenes.

Although other carbenes add stereospecifically to olefins, diphenylmethylene exhibits radical properties (71) and its addition to olefins is non-stereospecific (32). This observation suggests that the two free electrons of the divalent carbon are unpaired. A similar observation was made with propargylene
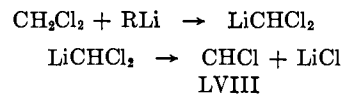
$$H-C{\equiv}C-\ddot{C}-H \;\leftrightarrow\; H-\ddot{C}-C{\equiv}C-H$$
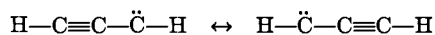
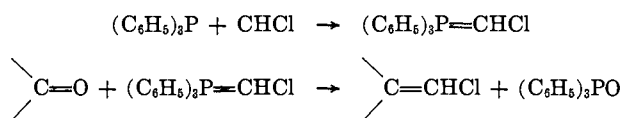which appears to react as though it were a free radical (119).

D. CHLOROMETHYLENE

1. Preparation and Reactions

Chloromethylene (LVIII) is prepared by the action of methyllithium (15a), n-butyllithium (15, 113), or phenyllithium (113) on methylene chloride in dry ether.

$$CH_2Cl_2 + RLi \;\rightarrow\; LiCHCl_2$$
$$LiCHCl_2 \;\rightarrow\; CHCl + LiCl$$
$$\text{LVIII}$$

It appears that n-butyllithium is a better base than phenyllithium for the preparation of chlorocarbene. Reaction with n-butyllithium in the presence of triphenylphosphine gives a yield of 65% of triphenylphosphinechloromethylene as compared with that of 40% yield when phenyllithium is used to generate the carbene (113).

The reaction of chloromethylene with triphenylphosphine to produce the ylide triphenylphosphinechloromethylene is of importance, because the latter undergoes the Wittig reaction in the presence of aldehydes or ketones to give substituted vinylidene chlorides (113).

$$(C_6H_5)_3P + CHCl \;\rightarrow\; (C_6H_5)_3P{=}CHCl$$

$$\underset{/}{\overset{\backslash}{}}C{=}O + (C_6H_5)_3P{=}CHCl \;\rightarrow\; \underset{/}{\overset{\backslash}{}}C{=}CHCl + (C_6H_5)_3PO$$

Chloromethylene, an electrophilic reagent, reacts with olefinic double bonds to form chlorocyclopropanes, the yield depending on the nucleophilicity of the olefins (15, 16).

$$CH_2Cl_2 + n\text{-}C_4H_9Li \;\rightarrow\; LiCHCl_2 \;\rightarrow\; CHCl + LiCl$$
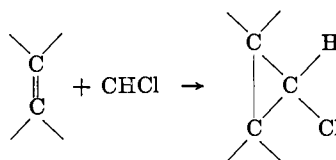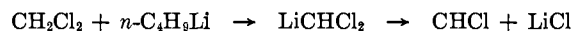
2,3-Dimethyl-2-butene gives 67% of 1-chloro-2,2,3,3-tetramethylcyclopropane, trans-2-butene gives 40% of 1-chloro-2,3-trans-dimethylcyclopropane, and cyclohexene 31% of two stereoisomeric 7-chlorobicyclo[4.1.0] heptanes (LIX) and (LX) in a ratio 1:2, both reduced with sodium in liquid ammonia to give bicyclo[4.1.0] heptane (14).

LIX   LX
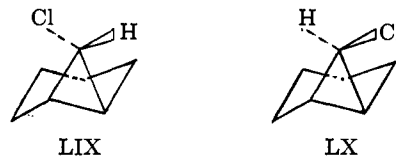
However, in the absence of an olefin, chloromethylene adds to butyllithium to yield 1-chloro-n-amyllithium (LXI), which undergoes α-elimination and forms 1-pentene by a hydride anion shift (14, 15).

$$CH_2Cl_2 + n\text{-}C_4H_9Li \;\rightarrow\; LiCHCl_2 \;\rightarrow\; CHCl + LiCl$$

$$C_3H_7CH{=}CH_2 + LiCl \qquad\qquad \text{LXI}$$
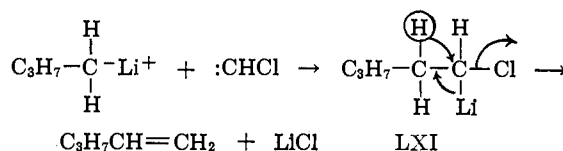
2. Ring Expansions

Chloromethylene has been found useful for the ring expansion of heterocyclic and aromatic systems.

When dihydropyran (XX) was left to react with the carbene, the *endo* and *exo* racemic mixtures of 2-oxa-7-chloronorcarane (LXII) were obtained in a ratio of 1:1.5 (110).
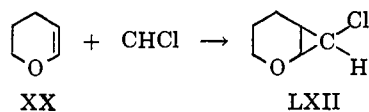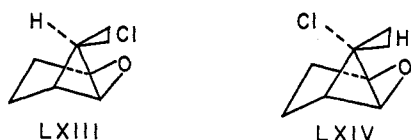

XX   LXII

The predominant isomer has been assigned structure LXIII, while the other isomer has structure LXIV. This shows that the formation of LXIV is hindered in the transition stage due to the eclipsing of the ring by


LXIII   LXIV

the large chlorine atom of chloromethylene, while the effect of the relatively small hydrogen atom is less pronounced and the isomer LXIII forms faster. Thus, the isomer LXIII is the *exo*-2-oxa-7-chloronorcarane and the isomer LXIV is the *endo* compound.

The application of heat on the isomer LXIV leaves it unaffected. It can be distilled at atmospheric pressure unchanged. When the isomer LXIII is heated, it decomposes at 120° at atmospheric pressure, or undergoes ring expansion to give 2,3-dihydroöxepine (LXV) when distilled from quinoline at reduced pressure.


LXV
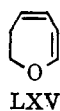
The ease with which the isomer LXIII is converted to LXV is due to anchimeric assistance by the *trans*-oxygen atom during the loss of the chlorine atom.

Both isomers LXIII and LXIV are reduced easily with sodium in liquid ammonia to give 70 and 60% yields, respectively, of 2-oxanorcarane (LXVI).
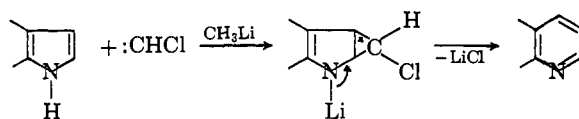

LXVI
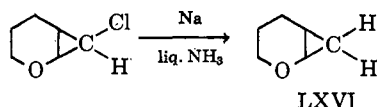
Although the reaction of dichloromethylene and phenols generally leads to substitution products (135, 149), chloromethylene is a better electrophile and reacts with aromatic compounds effecting ring expansion. When chloromethylene is prepared from methylene chloride and methyllithium, it reacts in the presence of lithium phenolates to form tropones (LXVII) (15a).

$$CH_2Cl_2 + CH_3Li \rightarrow CHCl$$

LXVIIa, R_1, R_2 = H
b, R_1 = H, R_2 = CH_3
c, R_1, R_2 = $(CH_3)_3C$
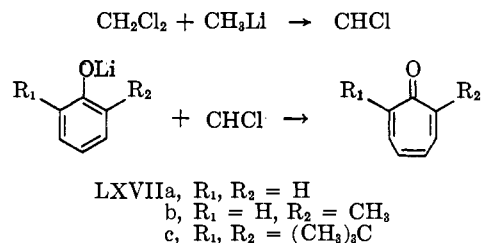
These transformations represent the first examples of one-step conversions of monocyclic benzenoid systems to the corresponding tropenoid. In particular, the 2,7-dibutyltropone is isolated in yields as high as 70%.

Chloromethylene adds also to the rings of pyrrol and indole to give the expanded products pyridine (32%) and quinoline (13%), respectively (16a).

E. FLUORENYLENE AND CYCLOPENTADIENYLENE

The decomposition of 9-dimethylsulfonium fluorenylide has been shown to give as an intermediate reaction product fluorenylene (LXVIII) (64).

LXVIII
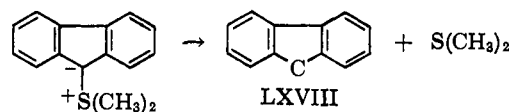
In a similar way, other dimethylsulfonium compounds have been decomposed to give the corresponding carbenes. For instance, *p*-nitrobenzyldimethylsulfonium *p*-toluenesulfonate decomposes in the presence of sodium hydroxide at 60° to form the *p*-nitrobenzyl carbene (LXIX) from which a mixture of *cis*- and *trans*-
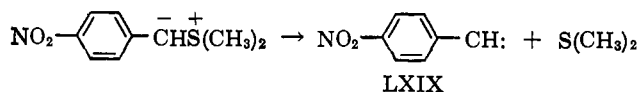
LXIX

p,p'-dinitrostilbenes is obtained by dimerization of the carbene LXIX (129).

The decomposition of these sulfonium compounds is the reverse of the coupling of carbenes with nucleophilic agents.

It has been proved (33) that 9-trimethylammonium fluorenylide (LXX) also decomposes into LXVIII,

LXX
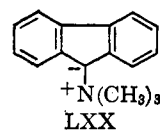
followed by its subsequent reactions with other amines (4, 33).
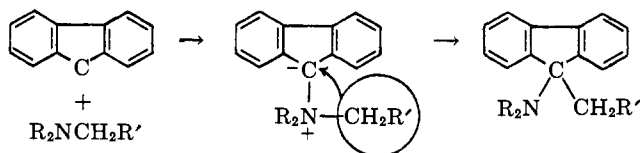
Fluorenylene reacts with oxygen to form fluorenone (LXXI) or dimerizes to difluorenylidene (LXXII) (20).
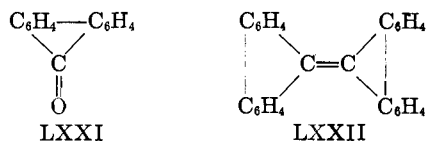
Although there is no evidence for the existence of the carbene cyclopentadienylene (LXXIII), the formation of fulvalene (LXXIV) by the photochemical decomposition of diazocyclopentadiene (LXXV) must proceed through the intermediate LXXIII, in a mechanism analogous to the formation of difluorenylidene (LXXII) (20).

LXXIII   LXXIV   LXXV

F. VINYLIDENE CARBENES

The rearrangement of an acetylenic to an allenic system or the reverse has been known for a long time. A careful study of this reaction with alkoxide or hydroxide ions appears to involve a vinylidene carbene (LXXVI)

where R is CH_3, C_6H_5, or H, and X is Cl, Br, OH, or $OCOCH_3$ (44).

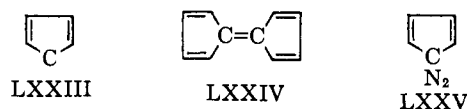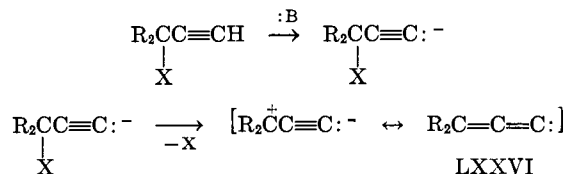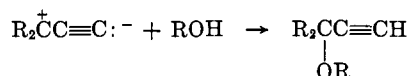The representation of vinylidene carbenes by a resonance hybrid is supported by the fact that in the presence of an alcohol they react in the propargyl form to produce a propargyl ether (62)

$$R_2\overset{+}{C}C\equiv C:^- + ROH \rightarrow R_2CC\equiv CH$$
$$\underset{OR}{|}$$

while in the presence of an olefin they react in the allenyl form to produce a cyclopropane (44, 45, 62).
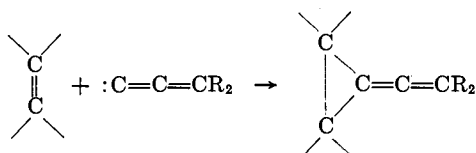
When propargyl bromide reacts with potassium t-butoxide in styrene, 1-ethynyl-2-phenylcyclopropane

(LXXVII) was isolated. The formation of this compound may have arisen by two paths; either through a vinylidene carbene (44)
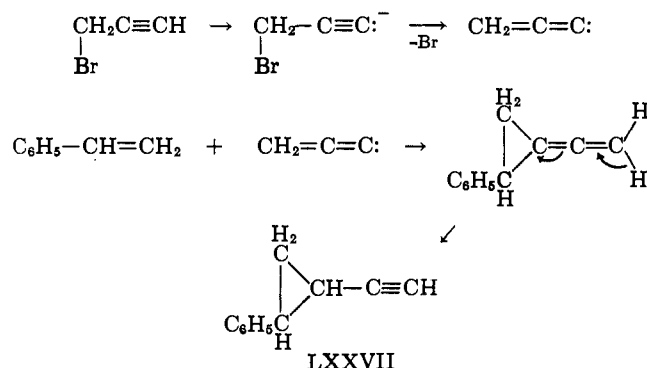
or through an α-elimination, and then addition to styrene (44).

$$C_6H_5-CH=CH_2 + :CH-C\equiv CH \rightarrow$$
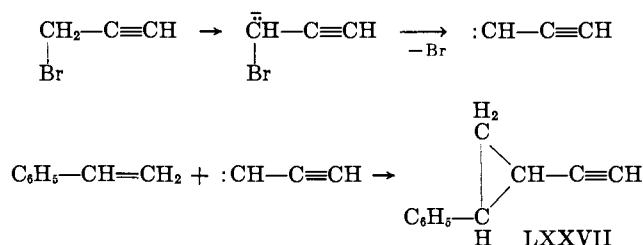
The addition of vinylidene carbenes to olefins is stereospecific and of the same order as in the case of the dihalomethylenes (45).

The earlier observation (11) that tetraarylhexapentaenes form in the reaction of diarylethynylcarbinols with acetic anhydride and potassium hydroxide in dry ether appears to involve a vinylidene carbene (44).

$$Ar_2C-C\equiv CH + (CH_3CO)_2O \xrightarrow{KOH}$$
$$\underset{OH}{|}$$

$$Ar_2C=C=C=C=C=CAr_2$$
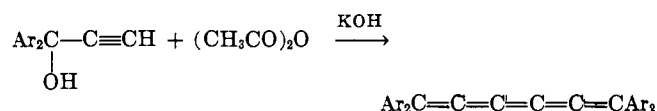
When diphenylethynyl acetate reacts with potassium t-butoxide, tetraphenylhexapentaene is obtained. The formation of tetraphenylhexapentaene is most likely to occur by reaction of diphenylvinylidene carbene with the anion of the acetylenic acetate which then loses the acetate group.

G. ALKYL CARBENES

As early as 1913, the preparation of alkyl carbenes was attempted by the decomposition of ketenes at temperatures as high as 650° (125). Free alkyl carbenes were not obtained; neither was evidence given of their intermediate formation. However, the formation of either their isomers or dimers in addition to carbon monoxide implies their existence.

Evidence of the formation of alkyl carbenes was given by reinvestigating (39, 40, 119a) the mechanism of the dehydrohalogenation of alkyl halides with strong bases

(18, 140, 141, 142, 143). The reaction proceeds *via*
alkyl carbenes, contrary to the belief of a γ-elimination
or a free radical mechanism.

This type of dehydrohalogenation was first observed
with the potassium amide dehydrochlorination of α,α-
dideuterio-*n*-octyl chloride, which while containing
1.98% deuterium, yielded 1-octene containing only
1.84% deuterium (49). Although the decrease in deu-

$$n\text{-}C_6H_{13}CH_2CD_2Cl \xrightarrow{\text{KNH}_2} n\text{-}C_6H_{13}CH=CD_2$$

terium content may be attributed to exchange reac-
tions, the data obtained with β,β-dideuterio-*n*-octyl bro-
mide cannot explain the high deuterium content of the
resulting olefin. These observations point to an α-
elimination and simultaneous shift of a β-hydrogen to
the α-position.

$$n\text{-}C_6H_{13}CH_2CH_2Cl \xrightarrow{\text{NH}_2^-} n\text{-}C_6H_{13}C\overline{H}_2CH\!-\!Cl \xrightarrow{-Cl}$$

$$n\text{-}C_6H_{13}CH\!-\!CH: \rightarrow n\text{-}C_6H_{13}CH=CH_2$$

If, however, a secondary or tertiary alkyl group is
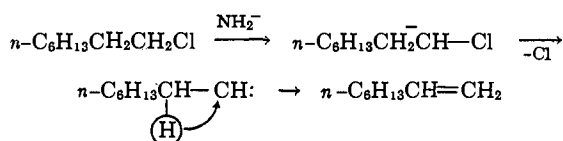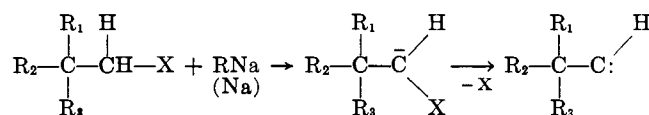attached to the α-carbon atom, the main products are
olefins and cyclopropanes formed from the carbene by
rearrangement and intramolecular insertion, respec-
tively (13, 37). The alkyl carbenes are formed by the
abstraction of an α-hydrogen and displacement of the
halide ion

where R_1 and R_2 are alkyls, R_3 being methyl or hydro-
gen, and R is alkyl, phenyl, amide, or methoxide. The
cyclopropanes and olefins form as shown
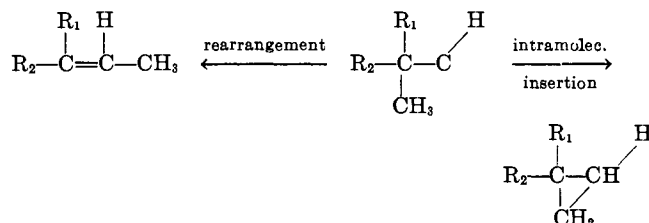
The formation of the alkyl carbenes is greatly af-
fected by steric interactions, as well as by the strength
of the base used to bring about the dehydrohalogena-
tion. Normal alkyl halides undergo a greater per-
centage dehydrohalogenation than the corresponding
isoalkyl halides, and sodium methoxide is less effective
than the stronger base phenylsodium.

Table VI shows the percentage dehydrohalogenation
of some alkyl halides with different bases.

It will be noted that the alkyl iodides react more
sluggishly than the bromides or the chlorides.

It has been found also that the *n*-propyl halides and

TABLE VI

PERCENTAGE DEHYDROHALOGENATION OF ALKYL HALIDES

	Alkyl Halides								Neo-hexyl[b]
	n-Butyl[a]			Isobutyl[a]			Neopentyl[b]		
Base	Cl	Br	I	Cl	Br	I	Cl	Br	Cl
PhNa	94	94	65	89	62	13	70	25	67
NaNH₂	30	15	—	7	1	—	60	—	—
NaOCH₃	10	—	—	0	—	—	—	—	—

a Ref. 39.   *b* Ref. 40.

n-amyl chloride react with phenylsodium to give cyclo-
propanes *via* carbene formation (13).

The formation of 1,1,2-triphenylethylene from 1,1,1-
triphenyl-2-chloroethane and amylsodium, in inert sol-
vents, shows a close analogy to the mechanisms postu-
lated above, in view of the fact a carbene is produced,
and the olefin forms by rearrangement (153).
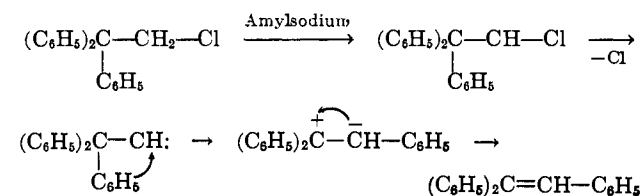
The same investigators have argued also about the
possibility that a carbanion is the main path to the ole-
fin, and rearrangement takes place during carbanion
formation.

In 1952, it was shown that tosylhydrazones react with
sodium in ethylene glycol to give diazo compounds (5).
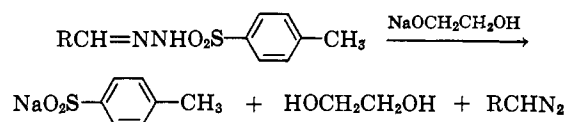
This new reaction has been widely used to produce
carbenes from the diazo compounds. Thus, tosylhy-
drazones of aromatic (36, 37), aliphatic (37, 100) and
alicyclic (38) aldehydes and ketones react with bases in
aprotic media, such as diethyl carbitol, $(C_2H_5OC_2H_4)_2O$,
to give diazo compounds, which on thermal decomposi-
tion at 160 to 220° generate the corresponding carbene.

The carbenes formed from the aliphatic tosylhydra-
zones undergo intramolecular insertion to give cyclo-
propanes, and hydrogen migration to give olefins. Hy-
drogen migration takes place mainly, rather than intra-
molecular insertion, in view of the fact that much
higher yields of olefins are obtained.

H. OXOCARBENES

The oxocarbenes are obtained from diazoketones* on

* Substances of this class can be made by the action of diazomethane upon
acid chlorides.

$$RCOCl + 2CH_2N_2 \rightarrow RCOCHN_2 + CH_3Cl + N_2$$

In the carrying out of the reaction, the acid chloride is added rapidly to at
least a twofold amount of diazomethane. If the reagents are added in the
reverse order, or if a smaller amount of diazomethane is used, the diazoketone
is destroyed by the hydrogen chloride which forms simultaneously. The
excess diazomethane serves to remove the hydrogen chloride as methyl
chloride and nitrogen.

irradiation, heating, or under the action of catalysts (Wolff rearrangement). Less certain is the formation of oxocarbenes in the Favorskii rearrangement, where an α-haloketone is dehydrohalogenated under the action of bases.

The oxocarbenes LXXVIII rearrange to form ketenes LXXIX

$$R-\overset{\overset{O}{\|}}{C}-CHN_2 \quad \rightarrow \quad R-\overset{\overset{O}{\|}}{C}-CH: \quad + \quad N_2$$
LXXVIII

$$\textcircled{R}-\overset{\overset{O}{\|}}{C}-CH: \quad \rightarrow \quad +\overset{\overset{O}{\|}}{C}-\underset{R}{CH} \quad \rightarrow \quad R-CH=C=O$$
LXXIX
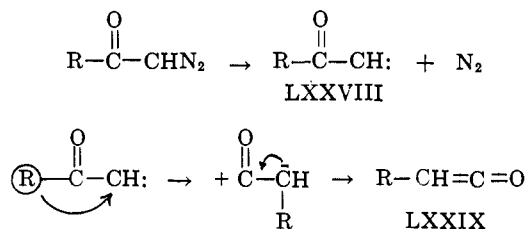
The ketene LXXIX is not ordinarily isolated from the reaction mixture, but its existence is demanded by the nature of the final products.

Here extensive analogy is observed to the Curtius, Stieglitz, and Hofmann rearrangements of nitrogen-containing compounds leading to the formation of carbene analogs which rearrange to the isocyanates.

The relative stability of oxocarbenes may arise by conjugation of the free electron pair with the carbonyl bond

$$R-\overset{\overset{O}{\|}}{C}-\overset{..}{C}H$$

When a cyclic diazoketone is decomposed, the rearrangement results in ring contraction. When diazonorcamphor (LXXX) is irradiated in methanol, methyl bicyclo[2.1.1]hexane-5-carboxylate (LXXXI) is obtained (144)

LXXX

LXXXI

Ring contraction has been observed also during the photochemical (85, 127), and thermal (151) decomposition of quinonediazides and diazonaphthalene oxides

and during the photochemical decomposition of diazopyridones (127a).
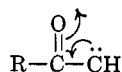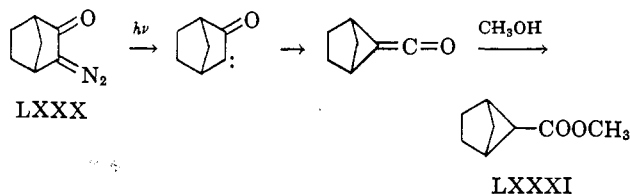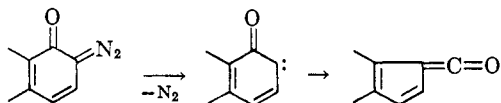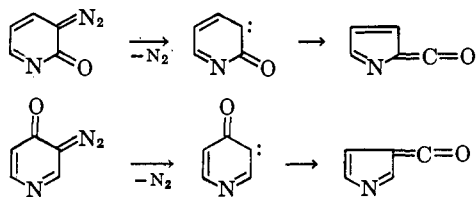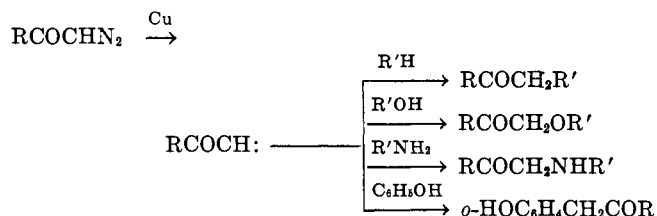

In the presence of water, the ketene LXXIX reacts to form an acid. An ester is produced in an alcohol, and an amide results when ammonia or an amine is used.

However, the copper-catalyzed decomposition of diazoketones does not give rearranged products (150). Instead, products are formed by the direct combination of the intermediate carbene with hydrocarbons, alcohols, amines and phenol.

$$RCOCHN_2 \xrightarrow{Cu}$$

RCOCH:
- $\xrightarrow{R'H}$ RCOCH$_2$R'
- $\xrightarrow{R'OH}$ RCOCH$_2$OR'
- $\xrightarrow{R'NH_2}$ RCOCH$_2$NHR'
- $\xrightarrow{C_6H_5OH}$ o-HOC$_6$H$_4$CH$_2$COR

An important feature of oxocarbenes is that no Walden inversion occurs in the migrating group R. This was more successfully shown from a study of the optically active diazoketones LXXXII (74) and LXXXIII (75), which resulted in the formation of optically active products of the same configuration.

$$n\text{-}C_4H_9-\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_5}{|}}{C}}-COCHN_2$$
LXXXII

LXXXIII
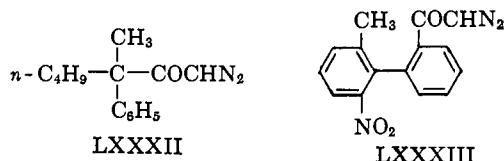
The rearrangement of the oxocarbenes has been used extensively for the synthesis of acids, where other methods involving a drastic reduction would interfere with the presence of a keto, nitro, lactone or other reducible group.

V. REFERENCES

(1) Anet, F. A. L., Bader, R. F. W., and Van der Auwera, A. M., J. Am. Chem. Soc., 82, 3217 (1960).
(2) Atkinson, B., and Atkinson, V. A., J. Chem. Soc., 2086 (1957).
(3) Badger, G. M., J. Chem. Soc., 3456 (1951).
(4) Bamford, W. R., and Stevens, T. S., J. Chem. Soc., 4675 (1952).
(5) Bamford, W. R., and Stevens, T. S., J. Chem. Soc., 4735 (1952).
(6) Banhoeffer, K. F., Geib, K. H., and Reitz, O., J. Chem. Phys., 7, 664 (1939).
(7) Barrow, R. F., Pearson, T. G., and Purcell, R. H., Trans. Faraday Soc., 35, 880 (1939).
(8) Bawn, C. E. H., and Milsted, J., Trans. Faraday Soc., 35, 889 (1939).
(9) Bergmann, E., Ber., 62, 893 (1929).
(10) Burton, M., Davis, T. W., Gordon, A., and Taylor, H. A., J. Am. Chem. Soc., 63, 1956 (1941).
(11) Cadiot, P., Ann. Chim., [13] 1, 214 (1956).
(12) Chambers, R. D., Clark, H. C., and Willis, C. J., J. Am. Chem. Soc., 82, 5298 (1960).
(13) Closs, G. L., Abstracts of Papers, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1960, p. 9-P.

(14) Closs, G. L., and Closs, L. E., Abstracts of Papers, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1959, p. 4-P.

(15) Closs, G. L., and Closs, L. E., *J. Am. Chem. Soc.*, **81**, 4996 (1959).

(15a) Closs, G. L., and Closs, L. E., *J. Am. Chem. Soc.*, **83**, 599 (1961).

(16) Closs, G. L., and Schwartz, G. M., *J. Am. Chem. Soc.*, **82**, 5729 (1960).

(16a) Closs, G. L., and Schwartz, G. M., *J. Org. Chem.*, **26**, 2609 (1961).

(17) Clusius, K., and Douglas, A. E., *Can. J. Phys.*, **32**, 319 (1954).

(18) Condon, F. E., and Smith, D. E., *J. Am. Chem. Soc.*, **69**, 965 (1947).

(19) Dacey, J., and Hodgins, J., *Can. J. Research*, **28B**, 90 (1950).

(20) DeMore, W. B., Pritchard, H. O., and Davidson, N., *J. Am. Chem. Soc.*, **81**, 5874 (1959).

(21) Doering, W. von E., and Henderson, W. A., *J. Am. Chem. Soc.*, **80**, 5274 (1958).

(22) Doering, W. von E., and Hofman, A. K., *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(23) Doering, W. von E., and Knox, L. H., *J. Am. Chem. Soc.*, **73**, 828 (1951).

(24) Doering, W. von E., and Knox, L. H., *J. Am. Chem. Soc.*, **75**, 297 (1953).

(25) Doering, W. von E., and Knox, L. H., *J. Am. Chem. Soc.*, **78**, 5447 (1956).

(26) Doering, W. von E., and LaFlamme, P. M., *Tetrahedron*, **2**, 75 (1958).

(27) Doering, W. von E., Buttery, R. G., Laughlin, R. G., and Chanduri, N., *J. Am. Chem. Soc.*, **78**, 3224 (1956).

(28) Douglas, A. E., *Astrophys. J.*, **114**, 466 (1951).

(29) Duchesne, J., and Burnelle, L., *J. Chem. Phys.*, **21**, 2005 (1953).

(30) Duffey, G. H., *J. Chem. Phys.*, **17**, 840 (1949).

(31) Emschwiller, G., *Compt. rend.*, **188**, 1555 (1929).

(32) Etter, R. M., Skovronek, H. S., and Skell, P S., *J. Am. Chem. Soc.*, **81**, 1008 (1959).

(33) Franzen, V., *Ber.*, **93**, 557 (1960).

(34) Frey, H. M., *Proc. Roy. Soc.* (London), **A251**, 575 (1959).

(35) Frey, H. M., *J. Am. Chem. Soc.*, **82**, 5947 (1960).

(36) Friedman, L., Abstracts of Papers, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1959, p. 4-P.

(37) Friedman, L., and Shechter, H., *J. Am. Chem. Soc.*, **81**, 5512 (1959).

(38) Friedman, L., and Shechter, H., *J. Am. Chem. Soc.*, **82**, 1002 (1960).

(39) Friedman, L., and Berger, J. G., *J. Am. Chem. Soc.*, **83**, 492 (1961).

(40) Friedman, L., and Berger, J. G., *J. Am. Chem. Soc.*, **83**, 500 (1961).

(41) Guether, A., *Ann.*, **123**, 121 (1862).

(42) Gutsche, C. D., and Hillman, M., *J. Am. Chem. Soc.*, **76**, 2236 (1954).

(43) Harrison, A. G., and Lossing, F. P., *J. Am. Chem. Soc.*, **82**, 1052 (1960).

(44) Hartzler, H. D., *J. Am. Chem. Soc.*, **83**, 4990 (1961).

(45) Hartzler, H. D., *J. Am. Chem. Soc.*, **83**, 4997 (1961).

(46) Herzberg, G., *Rev. Mod. Phys.*, **14**, 195 (1942).

(47) Herzberg, G., *Astrophys. J.*, **96**, 314 (1942).

(48) Herzberg, G., and Shoosmith, J., *Nature*, **183**, 180 (1959).

(49) Hill, D. G., Judge, W. A., Skell, P. S., Kantor, S. W., and Hauser, C. R., *J. Am. Chem. Soc.*, **74**, 5599 (1952).

(50) Hine, J., *J. Am. Chem. Soc.*, **72**, 2438 (1950).

(51) Hine, J., and Burske, N. W., *J. Am. Chem. Soc.*, **78**, 3337 (1956).

(52) Hine, J., and Dowell, A. M., Jr., *J. Am. Chem. Soc.*, **76**, 2688 (1954).

(53) Hine, J., and Duffey, D. C., *J. Am. Chem. Soc.*, **81**, 1129 (1959).

(54) Hine, J., and Duffey, D. C., *J. Am. Chem. Soc.*, **81**, 1131 (1959).

(55) Hine, J., and Langford, P. B., *J. Am. Chem. Soc.*, **79**, 5497 (1957).

(56) Hine, J., and Porter, J. J., *J. Am. Chem. Soc.*, **79**, 5493 (1957).

(57) Hine, J., and Tanabe, K., *J. Am. Chem. Soc.*, **79**, 2654 (1957).

(58) Hine, J., Burske, N. W., Hine, M., and Langford, P. B., *J. Am. Chem. Soc.*, **79**, 1406 (1957).

(59) Hine, J., Dowell, A. M., Jr., and Singley, J. E., *J. Am. Chem. Soc.*, **78**, 479 (1956).

(60) Hine, J., Ketley, A. D., and Tanabe, K., *J. Am. Chem. Soc.*, **82**, 1398 (1960).

(61) Hine, J., Peek, R. C., and Oakes, B. D., *J. Am. Chem. Soc.*, **76**, 827 (1954).

(62) Jacobs, R. L., Abstracts of Papers, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1960, p. 65-P.

(63) Johnson, A. W., *J. Chem. Soc.*, 2352 (1951).

(64) Johnson, A. W., and LaCount, R. B., *J. Am. Chem. Soc.*, **83**, 417 (1961).

(65) Khalafawi, T. E., and Johannin-Gilles, A., *Compt. rend.*, **242**, 1716 (1956).

(66) Kharasch, M. S., Rudy, T., Nudenberg, W., and Büchi, G., *J. Org. Chem.*, **18**, 1030 (1953).

(67) Kistiakowsky, G. B., and Marshall, W. L., *J. Am. Chem. Soc.*, **74**, 88 (1952).

(68) Kistiakowsky, G. B., and Rosenberg, N. W., *J. Am. Chem. Soc.*, **72**, 321 (1950).

(69) Kopecky, K. R., Hammond, G. S., and Leermakers, P. A., *J. Am. Chem. Soc.*, **83**, 2397 (1961).

(70) Kosolapoff, G. M., "Organophosphorus Compounds," J. Wiley and Sons, Inc., New York, N. Y., 1950, pp. 23, 98.

(71) Krimse, W., Horner, L., and Hoffman, H., *Ann.*, **614**, 19 (1958).

(72) Laidler, K. J., and Casey, E. J., *J. Chem. Phys.*, **17**, 213 (1949).

(73) Laird, R. K., Andrews, E. B., and Barrow, R. F., *Trans. Faraday Soc.*, **46**, 803 (1950).

(74) Lane, J. F., and Wallis, E. S., *J. Am. Chem. Soc.*, **63**, 1674 (1941).

(75) Lane, J. F., and Wallis, E. S., *J. Org. Chem.*, **6**, 443 (1941).

(76) Langer, A., Hipple, J. A., and Stevenson, D. P., *J. Chem. Phys.*, **22**, 1836 (1954).

(77) Lennard-Jones, J., *Trans. Faraday Soc.*, **30**, 70 (1934).

(78) Lennard-Jones, J., and Pople, J. A., *Discussions Faraday Soc.*, **10**, 18 (1951).

(79) Letort, M., and Duval, X., *Compt. rend.*, **219**, 452 (1944).

(80) Löb, W., *Z. Elektrochem.*, **7**, 903 (1901).

(81) Maas, J., DeGaaff, G. B. R., and Denttertog, H. J., *Rec. trav. chim.*, **74**, 175 (1955).

(82) Margrave, J. L., and Wieland, K., *J. Chem. Phys.*, **21**, 1552 (1953).

(83) McDowell, C. A., and Warren, J. W., *Discussions Faraday Soc.*, **10**, 53 (1951).

(84) Miller, W. T., and Kim, C. S. Y., *J. Am. Chem. Soc.*, **81**, 5008 (1959).
(85) Möller, K., and Süs, O., *Ann.*, **612**, 153 (1958).
(86) Mossler, G., *Monatsh.*, **29**, 573 (1903).
(87) Mulliken, R. S., *Phys. Rev.*, **41**, 751 (1932).
(88) Mulliken, R. S., *Phys. Rev.*, **43**, 279 (1933).
(89) Nef, J. U., *J. Am. Chem. Soc.*, **26**, 1549 (1904).
(90) Niiva, K., and Oohata, K., *J. Phys. Soc. Japan*, **7**, 61 (1952).
(91) Parham, W. E., and Hasek, W. R., *J. Am. Chem. Soc.*, **76**, 935 (1954).
(92) Parham, W. E., and Koncos, R., *J. Am. Chem. Soc.*, **83**, 4034 (1961).
(93) Parham, W. E., and Loew, F. C., *J. Org. Chem.*, **23**, 1705 (1958).
(94) Parham, W. E., and Reiff, H. E., *J. Am. Chem. Soc.*, **77**, 1177 (1955).
(94a) Parham, W. E., Bolon, D. A., and Schweizer, E. E., *J. Am. Chem. Soc.*, **83**, 603 (1961).
(95) Parham, W. E., Reiff, H. E., and Swartzentruber, P., *J. Am. Chem. Soc.*, **78**, 1437 (1956).
(96) Parham, W. E., and Schweizer, E. E., *J. Org. Chem.*, **24**, 1733 (1959).
(97) Parham, W., E. and Twelves, R. R., *J. Org. Chem.*, **22**, 730 (1957).
(98) Park, J. D., Benning, A. F., Downing, F. B., Laucius, J. F., and McHarness, R. C., *Ind. Eng. Chem.*, **39**, 354 (1947).
(99) Pearson, T. G., Purcell, R. H., and Saigh, G. S., *J. Chem. Soc.*, 409 (1938).
(100) Powell, J. W., and Whiting, M. C., *Tetrahedron*, **7**, 305 (1959).
(101) Rice, F. O., *J. Am. Chem. Soc.*, **61**, 213 (1939).
(102) Rice, F. O., and Glasebrook, A. L., *J. Am. Chem. Soc.*, **55**, 4329 (1933).
(103) Richardson, D. B., Simmons, M. C., and Dvoretsky, I., *J. Am. Chem. Soc.*, **82**, 5001 (1960).
(104) Rodd, E. H., "Chemistry of Carbon Compounds," Vol. IIIB, Elsevier, Amsterdam, 1956, p. 1257.
(105) Rosenblum, C., *J. Am. Chem. Soc.*, **60**, 2819 (1938).
(106) Rupe, H., *Helv. Chim. Acta.*, **27**, 627 (1944).
(107) Sanderson, W. A., and Mosher, H. S., *J. Am. Chem. Soc.*, **83**, 5033 (1961).
(108) Sarkar, P. B., *Proc. Natl. Inst. Sci. India*, **2**, 63 (1936).
(109) Schenk, G. O., and Ziegler, H., *Naturwissenschaften*, **38**, 356 (1951).
(110) Schweizer, E. E., and Parham, W. E., *J. Am. Chem. Soc.*, **82**, 4085 (1960).
(111) Semeluk, G. P., and Bernstein, R. B., *J. Am. Chem. Soc.*, **76**, 3793 (1954).
(112) Semeluk, G. P., and Bernstein, R. B., *J. Am. Chem. Soc.*, **79**, 46 (1957).
(113) Seyferth, D., Grim, S. O., and Read, T. O., *J. Am. Chem. Soc.*, **82**, 1510 (1960).
(114) Simmons, H. E., and Smith, R. D., *J. Am. Chem. Soc.*, **80**, 5323 (1958).
(115) Simons, J. P., and Yarwood, A. J., *Nature*, **187**, 316 (1960).
(116) Skell, P. S., and Etter, R. M., *Chem. Ind.* (London), 624 (1958).
(117) Skell, P. S., and Garner, A. Y., *J. Am. Chem. Soc.*, **78**, 3409 (1956).
(118) Skell, P. S., and Garner, A. Y., *J. Am. Chem. Soc.*, **78**, 5430 (1956).
(119) Skell, P. S., and Klebe, J., *J. Am. Chem. Soc.*, **82**, 247 (1960).
(119a) Skell, P. S., and Krapcho, A. P., *J. Am. Chem. Soc.*, **83**, 754 (1961).
(120) Skell, P. S., and Sandler, S. R., *J. Am. Chem. Soc.*, **80**, 2024 (1958).
(121) Skell, P. S., Starer, I., and Krapcho, A. P., *J. Am. Chem. Soc.*, **82**, 5257 (1960).
(122) Skell, P. S., and Woodworth, R. C., *J. Am. Chem. Soc.*, **78**, 4496 (1956).
(123) Smith, L. G., *Phys., Rev.*, **51**, 263 (1937).
(124) Speziale, A. J., Marco, G. J., and Ratts, K. W., *J. Am. Chem. Soc.*, **82**, 1260 (1960).
(125) Staudinger, H., and Engle, R., *Ber.*, **46**, 1437 (1913).
(126) Stork, G., Abstracts of Papers, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961, p. 45-Q.
(127) Süs, O., and Möller, K., *Ann.*, **599**, 233 (1956).
(127a) Süs, O., and Möller, K., *Ann.*, **593**, 91 (1955).
(128) Swain, C. G., and Scott, C. B., *J. Am. Chem. Soc.*, **75**, 141 (1953).
(129) Swain, C. G., and Thornton, E. R., *J. Am. Chem. Soc.*, **83**, 4033 (1961).
(130) Tchakerian, A., *Bull. soc. chim.*, [4] **51**, 846 (1932).
(131) Thiele, J., and Dent, F., *Ann.*, **302**, 273 (1898).
(132) Urbain, G., *Bull. soc. chim.*, [4] **51**, 853 (1932).
(133) Urbain, G., *Bull. soc. chim.*, **53**, 647 (1933).
(134) Venkateswarlu, P., *Phys. Rev.*, **77**, 676 (1950).
(135) Verzele, M., and Sion, H., *Bull. soc. chim. Belges*, **65**, 627 (1956).
(136) Voge, H. H., *J. Chem. Phys.*, **16**, 984 (1948).
(136a) Wagner, W. M., *Proc. Chem. Soc.*, 229 (1959).
(137) Walborsky, H. M., and Pendleton, J. F., *J. Am. Chem. Soc.*, **82**, 1405 (1960).
(138) Waldron, J. D., *Trans. Faraday Soc.*, **50**, 102 (1954).
(139) Wawzonek, S., and Duty, R. C., *J. Electrochem. Soc.*, **108**, 1135 (1961).
(140) Whitmore, F. C., and Carney, T. P., *J. Am. Chem. Soc.*, **63**, 2633 (1941).
(141) Whitmore, F. C., Popkin, A. H., Bernstein, H. I., and Wilkins, J. P., *J. Am. Chem. Soc.*, **63**, 124 (1941).
(142) Whitmore, F. C., Popkin, A. H., and Pfister, J. R., *J. Am. Chem. Soc.*, **61**, 1616 (1939).
(143) Whitmore, F. C., and Zook, H. D., *J. Am. Chem. Soc.*, **64**, 1783 (1942).
(144) Wiberg, K. B., Lowry, B. R., and Colby, T. H., *J. Am. Chem. Soc.*, **83**, 3998 (1961).
(145) Winberg, H. E., *J. Org. Chem.*, **24**, 264 (1959).
(146) Woodworth, R. C., *Dissertation Abstr.*, **17**, 1201 (1957).
(147) Woodworth, R. C., and Skell, P. S., *J. Am. Chem. Soc.*, **79**, 2542 (1957).
(148) Woodworth, R. C., and Skell, P. S., *J. Am. Chem. Soc.*, **81**, 3383 (1959).
(149) Wynberg, H., *J. Am. Chem. Soc.*, **76**, 4998 (1954).
(150) Yates, P., *J. Am. Chem. Soc.*, **74**, 5376 (1952).
(151) Yates, P., and Robb, E. W., *J. Am. Chem. Soc.*, **79**, 5761 (1957).
(152) Zimmerman, H. E., and Paskovich, D. H., Abstracts of Papers, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961, p. 2-Q.
(153) Zimmerman, H. E., and Smentowski, F. J., *J. Am. Chem. Soc.*, **79**, 5455 (1957).