

Recent Progress in the Chemistry of Allenes.

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I. INTRODUCTION

The first allenic compound was found already in 1887. Up to near 1960, allenes received only limited attentions of organic chemists. In the last few years, however, several excellent review articles on this field were published,¹⁻⁶⁾ which brought hereafter a remarkable increase in the investigations concerning allenes.

The present review is intended to cover the reports on propadiene and substituted allenes which appeared in the period from the middle of 1968 to the end of 1971. The allene chemistry concerning transition metal compounds is separately described in chapter V. All reports on polyallenes and natural occurring allenes are excluded.

In the equations and Tables of this review, the following abbreviations are used: Me; methyl, Et; ethyl, Pr; propyl, Bu; butyl, Hex; hexyl, ϕ ; phenyl, Tol; tolyl, Adm; adamantyl, Ac; acetyl, Ts; tosyl, acac; acetylacetonate, Cp; cyclopentadienyl, THF; tetrahydrofuran, DMSO; dimethylsulfoxide, and HMPA; hexamethylphosphoric triamide. Hydrogens attached to carbons are usually omitted in equations and only the framework of carbon skeleton is described.

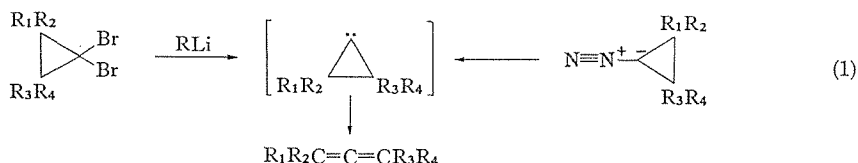
II. PREPARATIONS OF ALLENES

For the syntheses of allenes, Sandler and Karo's review⁶⁾ is recommended. The author wishes to describe the recent progress on the reaction for the synthesis and formation of allenes with taking care to avoid duplication of the previous reviews.

II.1: Elimination Reactions

II.1.1 Synthesis of allenes *via* cyclopropylidene or their derivatives

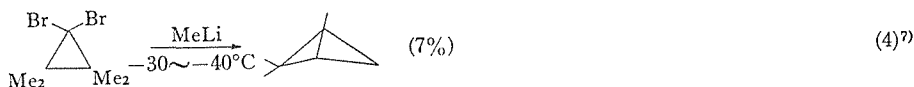
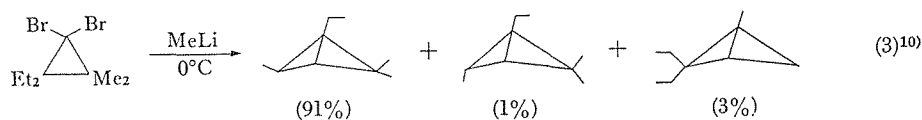
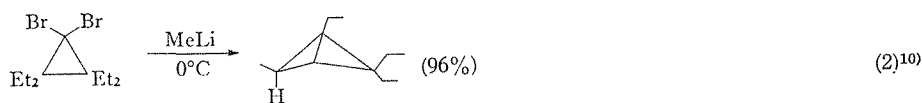
Allenes are synthesized by the rearrangement of carbene species obtained by the reaction of dibromocyclopropanes with alkyl lithium (generally methyl lithium) or by the decomposition of diazocyclopropanes (Eq. (1)).



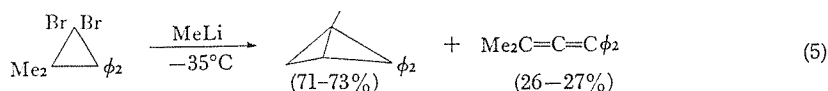
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Since only little contaminating by-products are accompanied in the reaction, many alkyl- or cycloalkyl-substituted allenes studied lately have been prepared by this route. Some new allenes such as diazoallene,¹⁹⁾ cyclopropylallene,²⁰⁾ and ferrocenylallene²¹⁾ are obtained by this method. In the presence of optically active (–)-separtine or chromous (+)-tartarate, partially optically active allenes are also obtained by this reaction.¹⁵⁾

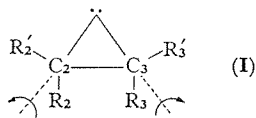
As for the intermediate stage of the reaction, it is shown that the reaction proceeds *via* a single precursor,⁷⁾ but it is not clear whether the precursor is a carbene^{7~10)} or a carbenoid.^{11~15)} The limitations of this synthetic method are as follows. a) Tetra-substituted allenes can not be prepared by the reaction of tetraalkyldibromocyclopropane and methyl lithium. The products are bicyclobutanes instead of allenes^{10,14,16,17)} (Eqs. (2)~(4)).



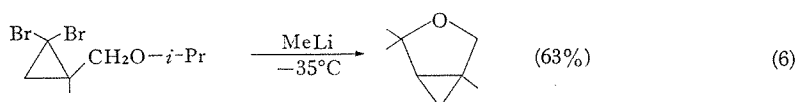
Tetra-substituted dibromocyclopropanes with some aryl substituents give cyclobutanes as the major products, and also allenes as the minor products (Eq. (5)).¹⁷⁾



The yield of allene is higher for anisyl-substituted cyclopropane (43%) than for phenyl-substituted cyclopropane. The formation of bicyclobutane takes place through the intramolecular insertion of carbene or carbenoid into the α -carbon-hydrogen bond of an alkyl substituent when the ring opening at the $\text{C}_2\text{-C}_3$ bond in **I** becomes slow because of the steric interaction of the substituents.^{14,17)}



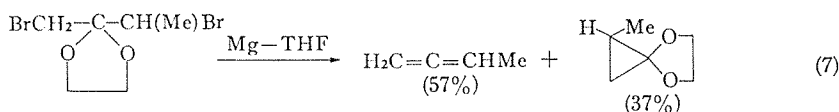
Aryl substituents facilitate the bond breakage of $\text{C}_2\text{-C}_3$ by stabilizing the state after the ring opening.¹⁷⁾ b) Allene are not obtained when some strain exists in the starting cyclopropanes.¹⁸⁾ c) The presence of reactive C-H bonds near to the carbene or carbenoid centre is unfavorable for the synthesis of allenes. Carbene species inserts into the C-H bond adjacent to ethereal oxygen to afford bicyclic compounds. Insertion is more facile at a tertiary carbon-hydrogen bond than at a secondary one.



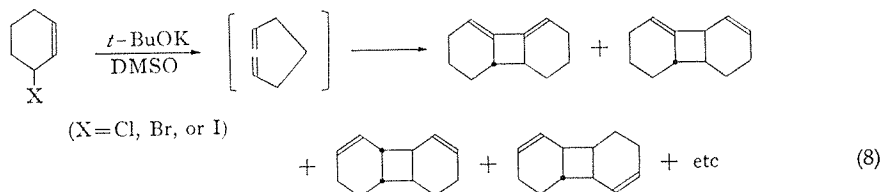
Insertion of atomic carbon into an ethylenic double bond is known as a method to prepare allene, and it also proceeds through a cyclopropylidene intermediate.¹³⁾ Butadiene is the major by-product.²²⁾ Stone *et al.* applied this method to the synthesis of fluoroallenes.²³⁾

II.1.2 Other eliminations

The reaction of substituted 1,3-dibromoacetone ethylene ketals with metallic Mg or Zn gives allenes²⁴⁾ (Eq. (7)).



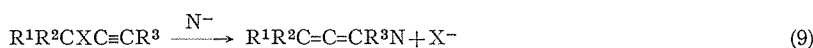
Haloallenes²⁵⁻³⁰⁾, higher cumulenes,³¹⁻³³⁾ and others^{34,35)} were synthesized from the corresponding starting materials by the elimination of hydrogen halides,^{25,26,29-32,34,35)} halogens,^{27,30)} or carbon monoxide²⁸⁾. The reagents used in these syntheses were sodium amide^{25,30)}, pyridine,³¹⁾ triethyl amine,³⁵⁾ alkali,^{26,29,32)} zinc,²⁵⁾ magnesium,²⁷⁾ and fluoride ion.²⁸⁾ The intermediacy of 1,2-cyclohexadiene was suggested in the reaction of 3-cyclohexenyl halides with potassium *t*-butoxide (Eq. (8))³⁶⁾



II.2: Rearrangements

II.2.1 Propargylic rearrangement

A number of groups (X) in the propargylic position of acetylenic compounds can be replaced by an S_N2' type reaction to give allene derivatives (Eq. (9)).

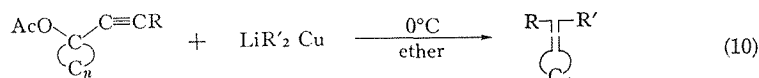


The competitive side reaction is an S_N2 type substitution, which gives acetylene derivatives. The ratio of two isomers is dependent on the steric situations of both reaction sites, C₁ and C₃;^{37,38)} tertiary substrates (R¹, R² = alkyl or aryl) generally give allenes, while primary substrates (R¹ = R² = H) acetylenes. The reaction product is also influenced by the nucleophilic reagent, the substituent, the leaving group and the reaction temperature.³⁹⁾

Hydroxyl group (X = OH in Eq. (9)) is replaced with hydrogen halides in the presence⁴⁰⁾ or absence⁴¹⁾ of cuprous salts, or lithium aluminium hydride^{42,43)} to give halo-

allenes and allenes, respectively. It was also replaced with phosphorous compounds.^{44,45)}

Ester and ether groups are better leaving groups than hydroxyl group and they are replaced even with Grignard reagents^{47,46,39)} or alkyl copper compounds^{48,49)} to give alkylated allenes or sometimes halogenated allenes in the case of Grignard reagents.⁵¹⁾ Thionyl chloride reacts with a propargyl ether to give an allene.⁵⁰⁾ Allenic alcohols are synthesized in good yields by the lithium aluminium hydride reduction of mono tetra-hydropyranoxy-derivatives of butyne-1,4-diols.⁵²⁾ The data of Rona and Crabbe for the preparation of allenylidene-cycloalkane is quoted in Table 1.

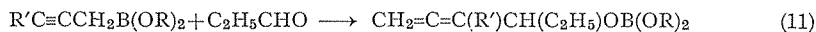
Table 1. Conversion of Ethynylcarbinol Acetates into Allenes.⁴⁹⁾

n	R	R'	Y (%)
4	H	Me	81
5	H	Me	85
6	H	Me	82
5	H	<i>n</i> -Bu	65
5	Me	Me	71
5	Me	<i>n</i> -Bu	80
5	<i>n</i> -Bu	Me	47

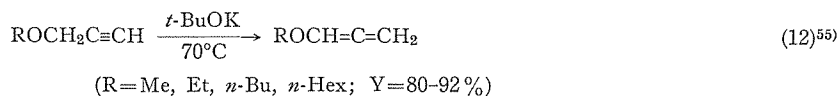
The lithium aluminium hydride reduction proceeds stereospecifically,³⁸⁾ but the reaction with organocopper reagents is nonstereospecific.⁴⁹⁾

Halogen atoms in the propargylic position is replaced by using lithium aluminium hydride,³⁷⁾ alkyl magnesium halides,^{53,54)} or triethylphosphite⁵⁵⁾ to give allenes, alkyl substituted³⁹⁾ allenes, or allenic phosphonates, respectively. A trimethylsilyl group in the propargylic position is replaced by SO₃ to give allenesulfonic acid trimethylsilyl ester.⁵⁶⁾

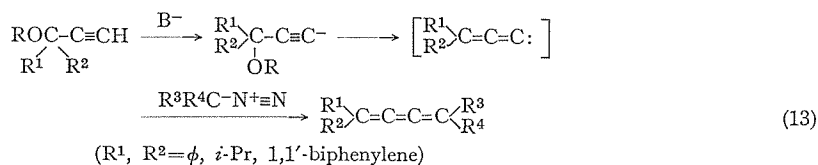
The reaction of dialkyl propargyl boronates with propionaldehyde (Eq. (11))⁵⁷⁾ might proceed also through an S_N2' type substitution reaction.



Propargyl ethers which have an acetylenic hydrogen react with bases to give allene derivatives⁵⁸⁻⁶⁰⁾ (Eq. (12)).

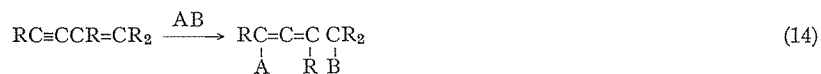


When there is no hydrogen in the propargylic position, the elimination of alkoxy group takes place to give an allenyl carbene,⁵⁹⁾ which can be trapped with a diazoalkane.



II.2.2 Other rearrangements

Allene is also prepared by the 1,4-addition to vinylacetylenes⁵¹⁻⁵⁹ (Eq. (14)).



Reagents corresponding to AB in Eq. (14) are lithium aluminium hydride,^{61,61a} bromine⁶¹, HSiR₃ or HGeR₃,^{63,64} HNR₂,⁶⁵⁻⁶⁷ alkyl lithium,⁶⁸⁻⁷⁰ aryl lithium,⁷¹ water,⁷² alcohol,⁷³ and organocalcium compounds.^{74a,74,75} The addition of alcohol is reversible and the reverse reaction proceeds successfully under basic conditions.⁷³

Another synthetic method of allenes is a thermal reaction similar to the Claisen rearrangement.⁷⁶⁻⁷⁸ A typical example is shown in Eq. (15) (Tab. 2).⁷⁶

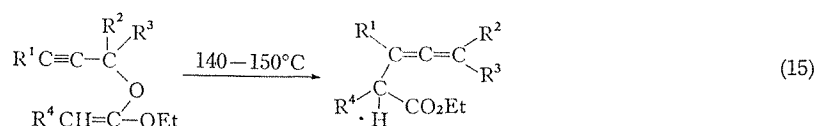
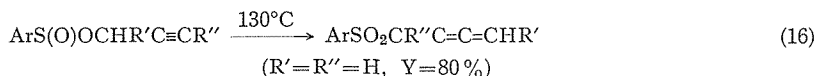


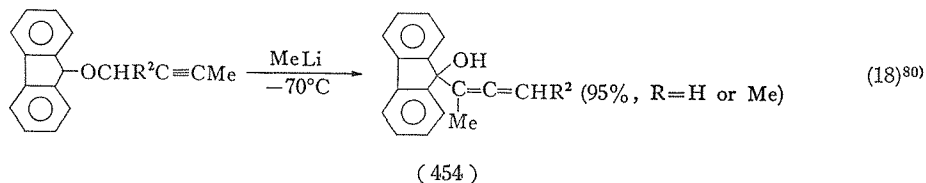
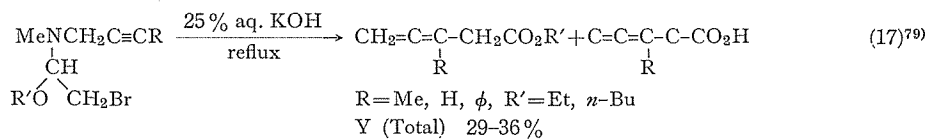
Table 2. Conversion of Prop-2-ynyl Alcohols into β -Allenic Esters.⁷⁶

R ¹	R ²	R ³	R ⁴	Y (%)
H	H	H	H	34
H	Me	H	H	63
H	<i>n</i> -Pr	H	H	60
H	Me	Me	Me	59
H	Me	Me	H	54
Me	Me	Me	H	61
H	-(CH ₂) ₅ -		H	61

Smith and Stirling studied the thermal rearrangement of sulfinates into sulfones and found that the reaction proceeds through an intramolecular cyclic transition state (Eq. (16)).⁷⁸



The base-catalyzed rearrangement of acetylenes is also used for the syntheses of allenes.^{79,80}



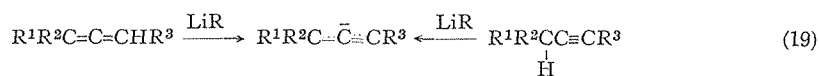
Propargyldiphenylthiophosphinite, which is formed by the reaction of $\text{Ph}_2\text{P}(\text{SCH}=\text{C}=\text{CH}_2)\text{Cl}$ and $\text{CH}\equiv\text{CCH}_2\text{SH}$ in the presence of triethylamine, rearranges to give an allene, $\text{Ph}_2\text{P}(\text{SCH}=\text{C}=\text{CH}_2)$.⁸¹⁾ Dimethylpropargyl sulfonium bromide also rearranges into an allenic isomer by the treatment with triethylamine in DMSO, or by being left in methanol.⁸²⁾

The pyrolytic isomerization of methylacetylene is also a known method for preparing propadiene. In the case of silica catalyst, the exchange of a hydrogen was observed between the reactant and catalyst.⁸³⁾ The reverse reaction, the isomerization of propadiene into methyl acetylene over zinc oxide, was studied by Chang and Kokes, and they found that the reaction proceeded through the co-ordination of a propargyl anion on the catalyst.⁸⁴⁾

Propargyl halides are reduced with tributyltin hydride to give mixtures of acetylenes and allenes. The yield of allene increases when an alkyl group is present at the propargylic carbon or when an alkyl group is absent at the acetylenic carbon. But allene is a minor product in any cases.⁸⁵⁾

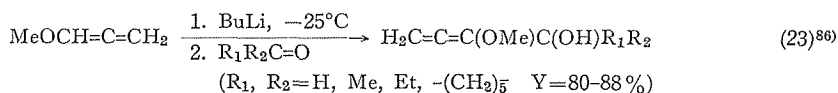
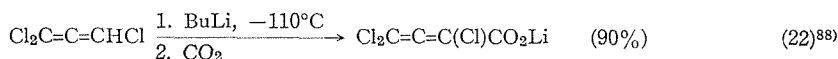
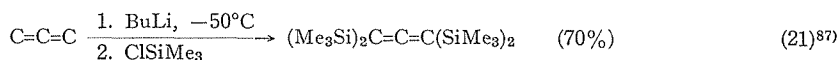
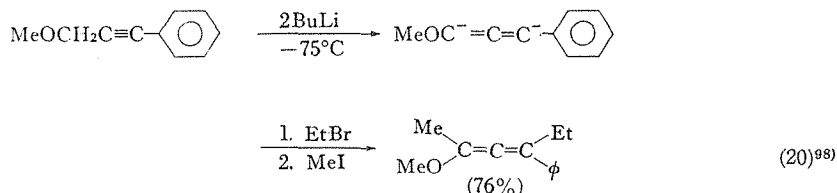
II.3: Synthesis of Allenes by Metallation

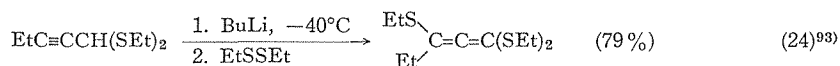
Allenic^{58,86-88)} or propargylic hydrogens⁷⁵⁻⁸⁰⁾ are abstracted by organo-lithium compounds to give the resonance stabilized allenic-acetylenic carbanion (Eq. (19)), which reacts with electrophilic reagents to yield allenes,^{58,86-91)} acetylenes,⁹⁵⁾ or their mixtures.⁹⁵⁻⁹⁸⁾



In general, butyl lithium is used as a lithium compound. Lithium amide might be used, but it is sometimes not reactive enough.⁸⁶⁾ Even when the reaction proceeds successfully with lithium amide, the products formed are complicated.⁵⁸⁾

The electrophiles reported are water,⁹⁸⁾ aldehydes,⁹⁸⁾ ketones,^{89,98)} alkyl and aryl halides,^{58,89,91,92)} trimethylchlorosilane,^{87,89-91)} carbon dioxide,^{88,94)} diethyl sulfate^{90,91,97)} and organic sulfur compounds.^{86,93)} The organolithium compound is oxidized by atmospheric oxygen.⁹⁹⁾ Typical examples are shown below:





A bromine atom in 1,1-dibromodiphenylallene similarly reacts with organolithium to give a monolithiated compound.⁹⁴⁾

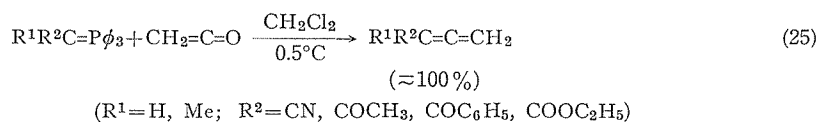
In the synthesis of phenyl-substituted allenes from phenyl-substituted dibromocyclopropane described in section II.1.1, an allenic hydrogen of the resulting allene is easily removed by the excess base to give carbanions, which react *in situ* with alkyl halides in the system to yield substituted allenes and/or acetylenes. Since it is difficult to prepare tetra-substituted allenes from tetra-substituted dibromocyclopropanes by the method of section II.1.1, the above reaction is a good synthetic method for tetra-substituted allenes.^{96, 100)}

Similar organometallic compounds are also prepared from propargyl halides and metals such as magnesium, zinc, or aluminium.^{101~106)} The additions of these organometallic compounds to ketones,^{102,103,105)} imines,¹⁰⁶⁾ and esters¹⁰⁴⁾ yield the corresponding derivatives of acetylenes and/or allenes, usually as their mixtures. The rate of addition to esters increases in the order of $\text{Zn} < \text{Mg} < \text{Al}$ ¹¹¹⁾ and the ratio of the resulting acetylenes and allenes depends on metals and substrates used. The Grignard reagents reacts with methyl borate to yield mixed boronates.¹⁰¹⁾ The stereospecificity of the products in the reaction of an optically active ketone, $\text{RCH}(\text{OCH}_3)\text{COCH}_3$, with such organometallics varies with the metal species used.¹⁰⁷⁾

II.4 Miscellaneous Methods

II.4.1 Wittig reaction

This method is, in general, not important in the synthesis of allenes, because the betaine intermediate included is rather stable and allene itself is unstable under the reaction conditions.¹⁰⁸⁾ By the use of stable ylids, however, terminal allenes are obtained in nearly quantitative yields.¹⁰⁹⁾



II.4.2 Hydroboration

Zweifel *et al.* reported a new synthetic method of terminal allenes *via* hydroboration (Eq. (26)).¹¹⁰⁾

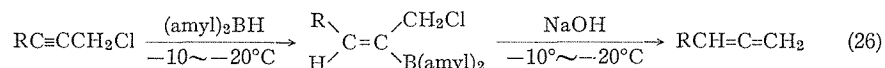


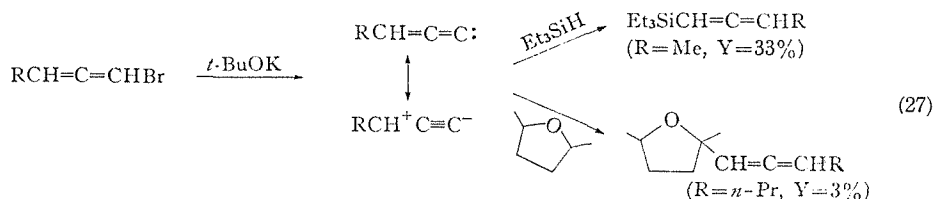
Table 3. Yields of Terminal Allenes Obtained from 1-Chloro-2-alkynes *via* Hydroboration-Elimination Reactions.¹¹⁰⁾

R	<i>n</i> -Bu	Cyclohexyl	<i>t</i> -Bu	Phenyl
Y (%)	83	93	92	91

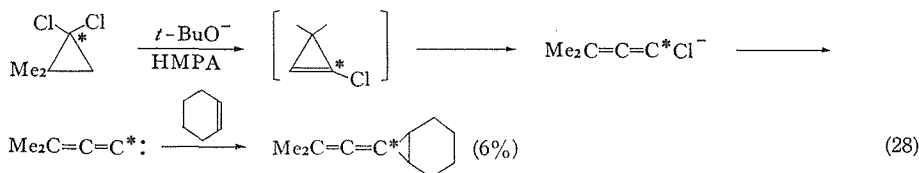
This method gives no by-products and the yield of allene is fair.

II.4.3 Methods by the use of carbene

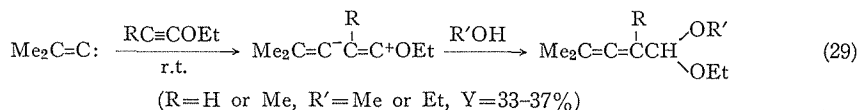
A treatment of bromoallene with potassium *t*-butoxide yields an intermediate vinylidene carbene, which inserts into a carbon-hydrogen bond or into a silicon-hydrogen bond to give allene.¹¹¹⁾



A vinylidene carbene is also formed from dichlorocyclopropane and a base *via* chlorocyclopropene.¹¹²⁾

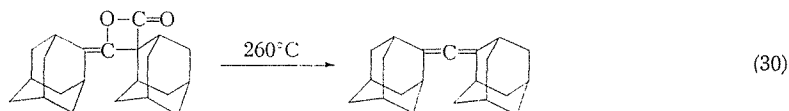


The reaction of an unsaturated carbene with an acetylene also gives allene.¹¹³⁾



II.4.4 Preparation of allenes by thermal- or photodecomposition

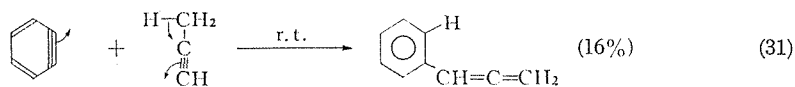
Bisadamantylidenemethane is obtained in a high yield by the thermal decomposition of adamantylidene ketone dimer (Eq. (30)).¹¹⁴⁾ The decomposition of a hydrazone¹¹⁵⁾ or an azalkane¹¹⁶⁾ yields some allenes as well as other products.



An allenic intermediate is suggested in the pyrolytic synthesis of spirodibenzocyclobutene.¹¹⁷⁾ Propadiene is found in the products of photo-decomposition of furfural,¹¹⁸⁾ furan,¹¹⁸⁾ thiophene,¹¹⁹⁾ or ethylene.¹²⁰⁾

II.4.5 Other methods

An ene reaction between photo-generated benzyne and methyl acetylene produces an allene.¹²¹⁾

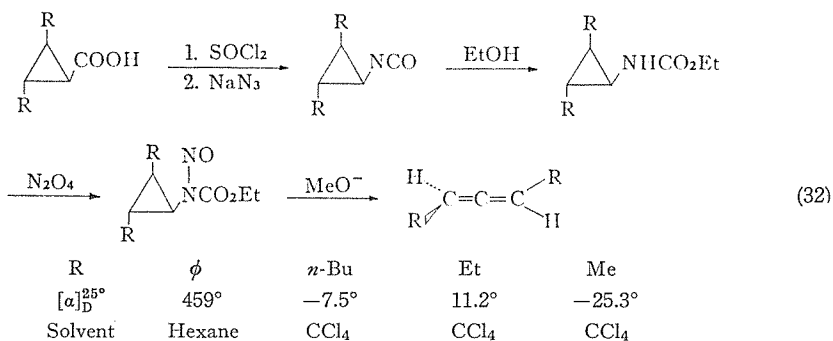


Other reports on the preparation of allenes describes the mercury-cathode-reduction of acetylenic or allenic halides,¹²²⁾ and the synthesis of bisamide of allene dicarboxylic acid by the reaction of 2 moles of aminoacetylene and carbon dioxide.¹²³⁾

II.5: Optically Active Allenes

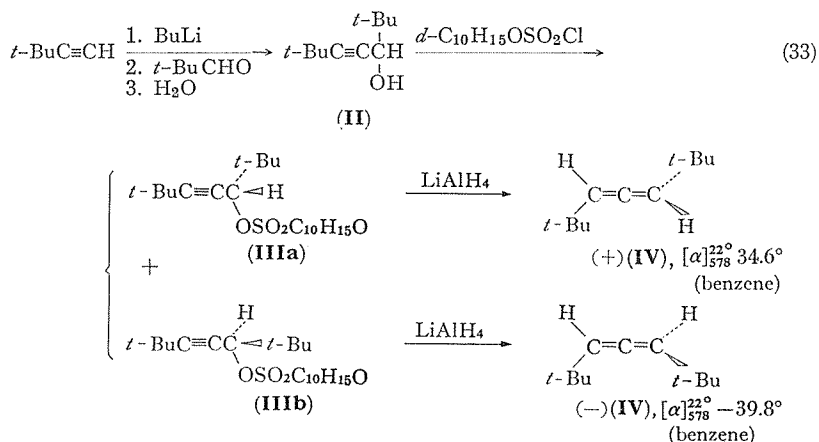
1,3-Disubstituted allenes have the property of molecular asymmetry and usually the racemic mixtures are obtained in syntheses. The preparations and properties of optically active allenes are summarized in this section.

Optically active aryl and alkyl allenes were synthesized *via* cyclopropylidene prepared from resolved 2,3-disubstituted cyclopropane carboxylic acids in 5 steps.¹²⁴⁾



(+) Penta-2,3-diene prepared from (+)-*trans*-2,3-dimethylcyclopropane-carboxylic acid has (*S*)-configuration.⁸⁾

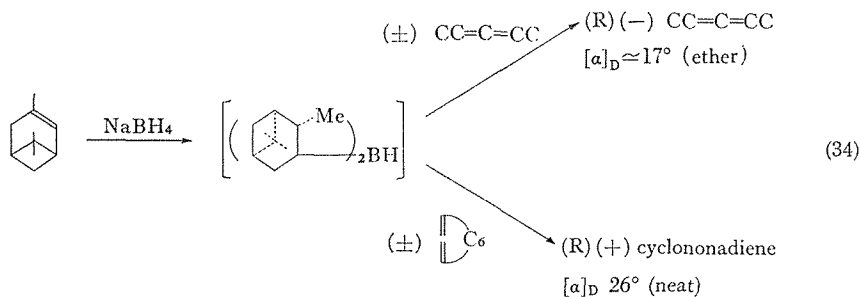
Corey *et al.* prepared optically active di-*t*-butylallene (**IV**) by the S_N2' type reduction of optically active propargyl esters.³⁸⁾



Partially optically active **IV** is obtained by the treatment of **II** with lithium aluminium hydride in the presence of aluminium chloride. The optical rotations of allenes obtained from optically pure (+) **II** and 2 moles of LiAlH₄ varies with the amount of AlCl₃, as follows.

AlCl ₃ (moles)	0.15	0.33	0.66
$[\alpha]_{578}^{22}$ (Benzene)	-32.9°	+5.4°	+26.4°

Caserio *et al.* found a simple method to obtain optically active allenenes. The hydroboration of racemic 1,3-disubstituted allenenes with optically active alkyl borane prepared *in situ* from sodium borohydride and (–)- α -pinene proceeds selectively, *i.e.*, one enantiomer reacts more rapidly, leaving an excess of the other enantiomer. They obtained partially optically active 2,3-pentadiene¹²⁵⁾ and 1,2-cyclononadiene by this method.¹²⁶⁾



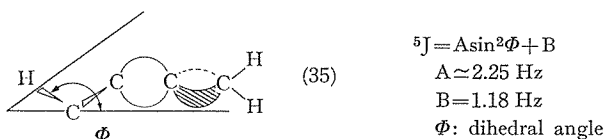
Cope *et al.* tried the partial resolution of 1,2-cyclononadiene by the use of (π -allene) dichloroplatinum(II) complex with an optically active amine ligand. They used α -methylbenzylamine or *p*-nitro- α -methylbenzylamine as the optically active amine and obtained 1,2-cyclononadiene of an optical purity of 44% by the treatment of fractionally crystallized allene complex with aqueous sodium cyanide.¹²⁷⁾

The absolute configuration of 1,2-cyclononadiene, the (*R*) configuration for the (+) enantiomer¹²⁸⁾ and the (*S*) configuration for the (–) enantiomer,¹²⁹⁾ is assigned separately by two groups. The sector rule for chiral allenenes is derived by Crabbe' *et al.*³⁰⁵⁾

III. PHYSICAL PROPERTIES OF ALLENES

Some spectroscopic properties of allenenes were studied lately, such as a microwave spectrum,¹³⁰⁾ electroic spectra,¹³¹⁻¹³³⁾ NMR spectra,¹³⁴⁻¹³⁶⁾ IR spectra,^{137,138)} and ESR spectra.^{139,140)} The characteristic IR absorption of allenenes appears at 1960 cm^{-1} for eight aromatic or heteroaromatic substituted allenenes¹³⁷⁾ and at 1950-1975 cm^{-1} for sixteen allenic alcohols of the type $(\text{CH}_3)_2\text{CHC}(\text{OH})=\text{C}=\text{CHCH}_2\text{R}$ ($\text{R}=\text{alkyl, aryl, cycloalkyl}$).¹³⁸⁾

A study of ¹³C NMR spectra of allenenes shows a linear relationship between the chemical shift of central carbon of allenic bond, δC_β , and the number and sort of the substituent.¹⁴¹⁾ A methyl substituent contributes +3.3 ppm to δC_β and an ethyl group contributes +4.8 ppm. There is another linear relationship between the chemical shifts of central (C_β) and terminal (C_γ) carbons of monosubstituted allenenes, $\text{C}_\gamma\text{H}_2=\text{C}_\beta=\text{C}_\alpha\text{HX}$. The inverse relation between δC_β and δC_γ is explained by the "extended" π -system of $\text{C}_\alpha\text{C}_\beta\text{C}_\gamma\text{HH}$ and $\text{C}_\gamma\text{C}_\beta\text{C}_\alpha\text{HX}$.¹⁴¹⁾ Nonequivalent two geminal allenic protons were reported for allenenes, $\text{RCHBrCOC}(\text{CH}_3)=\text{C}=\text{CH}_2$, which showed ABX_3 type spectra.¹³⁴⁾ Other allenenes, $\text{CH}_2=\text{C}=\text{CHCH}(\text{CH}_3)\text{CH}_2\text{R}$, ($\text{R}=\text{H, -OAc, -OTs}$) also showed complex absorptions due to the terminal methylenes, but this complication arose from a long range coupling through five bonds including an allenic bond.¹³⁶⁾ For the coupling constant of such a long range allenic coupling, the following equation was proposed.¹³²⁾



A negative sign of the geminal allenic coupling constant was verified experimentally.¹⁴²⁾ The sign is also negative for butatriene.¹⁴³⁾ NMR has been used for the conformational analysis of diphenylethylallene.¹⁴⁴⁾ ESR spectrum proved that the radicals generated from propadiene and methylacetylene by hydrogen abstraction are the same.^{139,140)}

Many reports on the theoretical treatment of propadiene have been published.¹⁴⁵⁻¹⁵⁰⁾ The strain energy,¹⁴⁸⁾ the molecular geometry¹⁵⁰⁾ and the energy barrier for rotation of bonds^{147,149)} are discussed. The ionization potential of propadiene is $9.53 \pm 0.03 \text{ eV}$.^{147,149-151)} Propadiene quenches the triplet excitation energy of benzene more effectively than ethylene does, but less effectively than propene.¹⁵²⁾ The solubility of propadiene into water containing cuprous chloride, ammonium chloride and hydrogen chloride is proportional to the partial pressure of propadiene over a range of 200-800 mmHg. The solubility of propadiene is about twice of that of methylacetylene.¹⁵³⁾

IV. REACTIONS OF ALLENES

IV.1: Cycloadditions

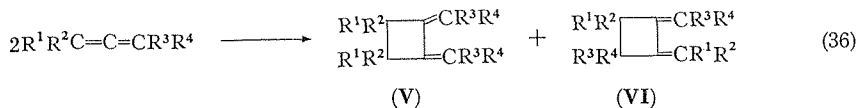
IV.4.1 Cyclodimerization of allenes

Dimerization of allenes to cyclobutane derivatives is a general reaction of allenes. Especially it is easy for polychloroallenes^{25,29,30,154-157)} such as trichloroallene or trichloroallenicarboxylic acid, tetrakis(methylthio)allene,⁹³⁾ perfluoro-1,2-pentadiene,²⁶⁾ and dimethylcyanoallene.¹⁵⁸⁾ These compounds tend to dimerize completely even below room temperature and are difficult to obtain in a pure state.

The orientation and stereochemistry of dimerisation of poly-substituted allenes have been studied extensively. Reported data on the regioscopic distribution of cyclobutanes show that the products are generally 1,2-dimethylenecyclobutanes and little reports are known which show the predominant formation of 1,3-dimethylenecyclobutanes.¹⁵⁹⁾ Which double bond takes part in the reaction is dependent on the substituents as seen from Table 4. As for the stereochemistry of substituents on the ring, the *trans* adducts are usually predominant,¹⁶⁰⁻¹⁶⁵⁾ but the *cis* adduct is obtained as the main product for the dimerization of 1,3-diphenylallene.¹⁶⁵⁾ The substituents on two exo-methylene groups locate mostly in syn positions.^{160,161,163,164,166)} Jacobs *et al.* proposed an orthogonal biradical intermediate for allene dimerization and explained the products from its stereochemical situations.^{160,166,167)}

The dimerization of optically active 1,2-cyclononadiene proceeds with about 100% of stereospecificity to give the meso product but it is not known whether the reaction proceeds through a concerted mechanism or a biradical one.¹⁶²⁾ The dimerization of optically active 2,3-pentadiene yields, however, the racemic products,¹⁶³⁾ suggesting a non-

Table 4. Cyclodimerizations of Unsymmetric Allenes.



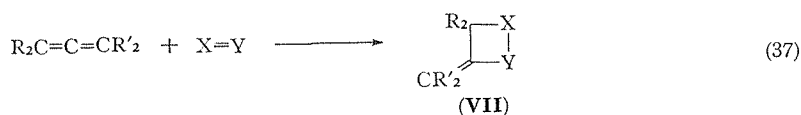
R ¹	R ²	R ³	R ⁴	Temp. (°C)	Y (%)	Product (%)		Reference
						V	VI	
Cl	Cl	Cl	CO ₂ Et	-90~20	100	100		155, 29
Cl	Cl	Cl	H	20	100			25
Cl	Cl	Cl	Br	r.t.	100	100		30
F	F	F	C ₂ F ₅	20	85	26	74	26
H	CN	Me	Me	85			100	158
H	CN	Me	Et	130	100		100	158
H	H	H	Cl	60		100		167
Me	Me	H	Cl	80~90		100		167
φ	H	H	Cl	80	30~45	41	59	166
Adm	H	H	Cl	125~130	90	59	41	160
H	H	H	Me	170	29	54	46	161
φ	φ	H	Cl			4 : 5		165
φ	φ	H	Br			4 : 5		165
φ	φ	φ	Me	150	39	100		168

concentrated process. Dolbier, Jr. and Dai examined the secondary isotope effect for the dimerization of propadiene. The intermolecular isotope effect (k_H/k_D) is 1.013 ± 0.020 and the intramolecular value is 1.14 ± 0.020 , which suggest the reaction passes through more than two energy barriers.³⁰⁶ These data are favorable for a biradical mechanism.

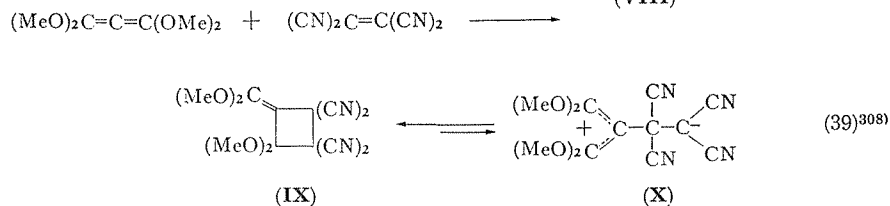
Detzer and Roedig studied the kinetics of dimerization of polyhalogenated allenenes. The reaction followed second order kinetics and showed large and negative entropies of activation and relatively small enthalpies of activation. They detected no paramagnetic species during the dimerization of tetrachloroallene, and proposed a non-concerted two-step mechanism.¹⁵⁹

IV.1.2 (2+2) Cycloadditions of allenenes with unsaturated compounds other than allenenes

This cyclization is also a well-known reaction, and usually yields four-membered cyclic compounds (Eq. (37)).



When an electron-rich allene and an electron deficient unsaturated compound are used as the reactants, the reaction yields an equilibrium mixture of a zwitter-ion and a four membered-cyclic compound, or only the former ion.^{307,308}

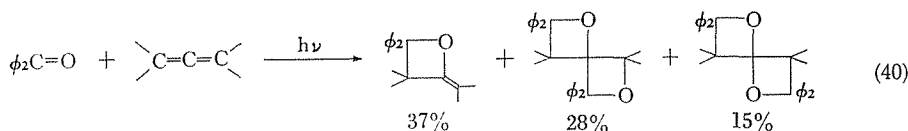


The cycloaddition is sometimes accompanied by an ene reaction.^{28,170,172,174,309}

Concerning to the mechanism of the thermal (2+2) cycloaddition, the above-mentioned two mechanisms are still the objects of discussion. Contrary to the dimerization of allenes, Baldwin *et al.* obtained optically active products from the reaction of optically active 2,3-pentadiene and acrylonitrile. They explained the results from the steric requirement in the intermediate.¹⁷¹ The reaction of allene with tetrafluoroethylene or fluorochloroethylene is explained successfully by a biradical mechanism.^{310,169}

Kiefer and Okamura studied the reaction of 3-methyl-1,2-butadiene with dimethyl maleate or fumarate and found that these reactions are stereospecific. Fumarate gives only the *trans* adduct. They also tried the kinetic study, and concluded that this reaction does not proceed *via* a biradical intermediate.¹⁷²

As a photo-cycloaddition, the reaction of allenes with ketones¹⁷³ or thioketones^{174,175} has been reported. Reaction with ketone yields a 2-methylene-oxacyclobutane, two 1:2 adducts, a spiroketal and a dioxaspiroalkane, and sometimes a cyclobutanone, the rearranged product of an oxetane.

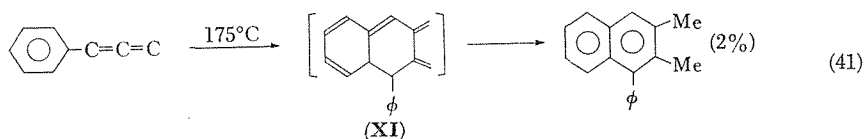


In the case of the addition of 1,4-benzoquinone or 1,4-naphthoquinone with tetramethylallene, the product is exclusively a rearranged one, derivative of 5-hydroxyindane-2-one.¹⁷⁶

Benzyne also reacts with electron-rich allenes to give bicyclic compounds but an ene reaction is in competition with the cycloaddition (Table 8).¹⁷⁷ Allenes with electron-releasing substituents are favorable to cycloaddition.

IV.1.3 (2+4) Cycloadditions

Allenic compounds react as dienophiles,^{86,154,178,179} while α,β -unsaturated allenic compounds react as diene.^{180,181} In the dimerization of phenyl allene, one allene molecule acts as a diene and another molecule as a dienophile (Eq. (41)).¹⁸²



The examination of the secondary isotope effect (k_H/k_D) is found to be effective to distinguish either a concerted process or a two-step one.¹⁸³⁾ The secondary isotope effect for the reaction of hexachlorocyclopentadiene with 1,1-dideuteroallene is 0.90, supporting the one-step mechanism, and the value for the cycloaddition reaction of acrylonitrile with 1,1-dideuteroallene is 1.21, suggesting the two-step biradical mechanism. The one-step concerted mechanism is proposed for the reaction of allene with tetracyanoethyleneoxide by this isotope effect.¹⁸⁴⁾

Table 5. Isotope Effects for Allene Cycloadditions.¹⁸⁴⁾

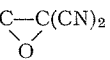

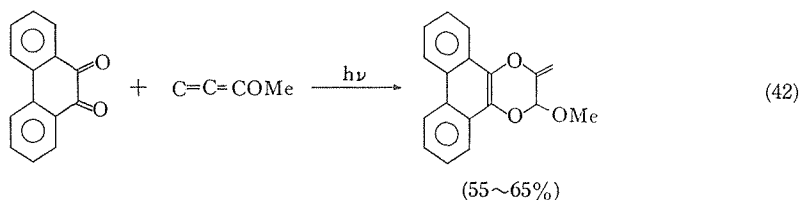
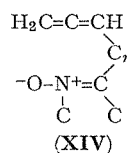
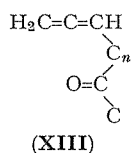
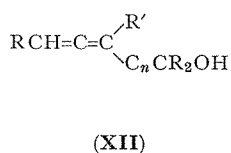
Type of Reaction	Reagent	k_H/k_D
2+2	allene	1.14 ± 0.02
2+2	acrylonitrile	1.21 ± 0.02
2+2	$F_2C=CCl_2$	1.15 ± 0.04
2+3	$(CN)_2C=C(CN)_2$ 	0.93 ± 0.01
2+4	 -Cl ₆	0.90 ± 0.03

Photo-induced (2+4) cycloaddition (Schönberg reaction) was applied to allenes.^{185,186)} In this reaction, a double bond of allene with an electron-releasing substituent is more reactive. A significant steric hindrance in the reaction of *t*-butylallene or 1,1-dimethylallene is confirmed kinetically.¹⁸⁶⁾

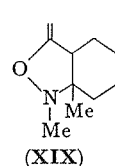
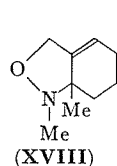
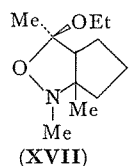
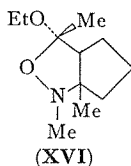
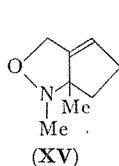


IV.1.4 Other cycloadditions

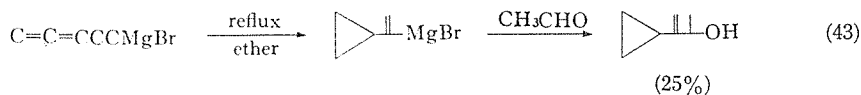
Some functional allenes react intramolecularly and yield cyclic products: Compounds **XII** rearrange to give cyclic unsaturated ether with basic catalyst in polar solvents.¹⁸⁷⁾ The derivatives of dihydrofuran are obtained when *n* was zero ($R=H$, $R'=OMe$, 60% yield). From **XII** ($n=1$, $R=H$, $R'=OMe$, SMe), methylenetetrahydrofuran or its rearranged product is produced. The acid-catalyzed reaction of these compounds gives different products.¹⁸⁸⁾ From **XII**, a ten-membered cyclic dimer is obtained when *n* is zero ($R=H$, $R'=OMe$). A six-membered unsaturated ether is formed when *n* is one ($R=H$, $R'=SMe$, 54% yield). Mercuric salts are good catalysts to yield the dihydrofuran derivatives ($n=0$, $R=Me-Pr$, 47~56% yield).¹⁸⁹⁾ The reaction of allenic ketones **XIII** with methylhydroxylamine hydrochloride yields nitrones **XIV**, which further undergo intramolecular cycloaddition.¹⁹⁰⁾



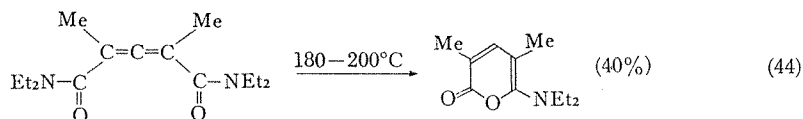
The structure of the resulting ring compounds is dependent on the number n ; when n is 2, **XV** is the product (45%), and when n is 3, **XVI**, **XVII**, and **XVIII** are isolated in 40, 16, and 40% yield, respectively. **XIX** is a sole product when n is 4.



An β -allenic grignard reagent rearranges to another Grignard reagent having a cyclopropyl group.¹⁹¹⁾

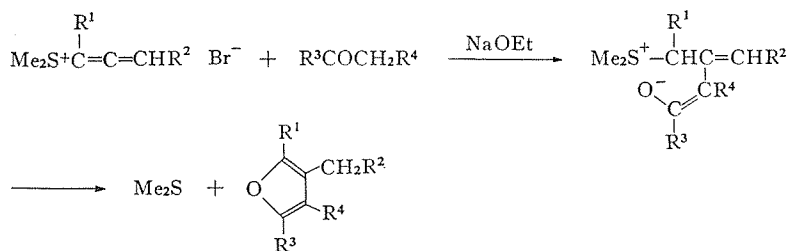


An allene dicarboxylic acid bisamide¹²³⁾ cyclizes to give an unsaturated lactone by heating.¹⁹²⁾



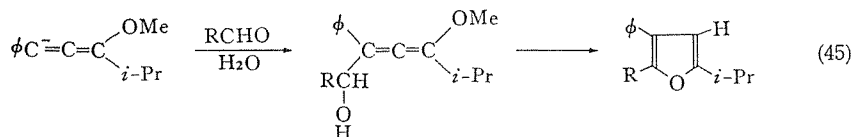
Epoxidation of a vinylallene is accompanied with the subsequent cyclization of the product to give cyclopenten-3-one.^{193,194)} Cyclo-1,2-nonadiene undergoes photorearrangement to give tricyclo(3.2.0)nonene.¹⁹⁵⁾ Substituted furans are synthesized in good yields by the reaction of allenic sulfonium halides with ketones.¹⁹⁶⁾

Table 6. Yields of Furans by the Addition of Enolate Anions to Allenic Sulfonium Salts.¹⁹⁶⁾



R ¹	R ²	R ³	R ⁴	Y (%)
H	H	Me	-CO ₂ Et	86
H	H	Me	-SO ₂ - <i>p</i> -Tol	78
H	H	ϕ	-CO ϕ	72
H	H	Me	-CO ϕ	89
H	H	Me/ ϕ	-CO ϕ /-COMe	83 (50/50 mix.)
H	ϕ	Me	-CO ₂ Et	63
Me	H	Me	-CO ₂ Et	61

Furans are also prepared from aldehydes and allenic compounds.



Similar reaction with ketones yields methylenedihydrofuran derivatives. Reaction of the carbanion with carbon dioxide yields an unsaturated lactone hemiacetal.¹⁹⁷⁾

Nitrogen-containing ring compounds such as pyrrolidinone,¹⁹⁸⁾ isoxazole,¹⁹⁹⁾ and oxazoline²⁰⁰⁾ derivatives are synthesized by the four-center addition of substituted allenes with azomethine oxide, phenylchloroaloxime, and azidoformate, respectively. Pyrazolines are produced by the reaction of allene with nitrile imine,²⁰¹⁾ arylsulphonyl azide,²⁰⁰⁾ or diazo alkanes.²⁰²⁻²⁰⁴⁾ The four-center reaction of 2-diazopropane with α,β -unsaturated allenes is influenced by steric and electronic factors, and the reaction occurs at the more electrophilic double bond of allenes. The electronically preferred product, 4-alkylidene-1-pyrazoline, is usually formed and the orientation is reversed in the case of crowded allenes.²⁰³⁾

Pyridones are synthesized by the Michael addition of ketoenamines to diethyl allene-dicarboxylate in fair to moderate yields.²⁰⁵⁾

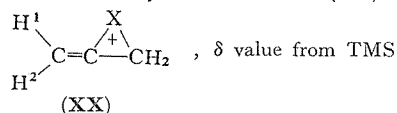
IV.2: Linear Addition Reactions

IV.2.1 Ionic addition

As for the addition of hydrogen chloride to allene, the intermediacy of a vinyl cation is suggested when bismuth chloride is used as a catalyst at -78°C .²⁰⁶⁾ In the case of phenylallene, however, it is shown that the addition of HCl occurs through a localized allylic cation, $\phi\text{C}^+\text{HCH}=\text{CH}_2$, at 30°C .²⁰⁷⁾ Methoxyallene reacts at -60°C in ether to yield 1-methoxy-3-chloropropene.¹⁸⁷⁾ For the HCl addition, the reactivity of allene is reported to be larger than that of cyclopropyl group.²⁰⁸⁾

As for the halogenation of allenes, Caserio *et al.* proved that halonium ion is a reasonable intermediate in the bromination and iodination of optically active allenes.¹²⁶⁾ The additions are stereospecific and give the *trans* adducts, but the optical purity of the iodination product of 2,3-pentadiene decreases significantly with the iodinating agent in the order $\text{ICl} > \text{IBr} > \text{I}_2$ owing to the participation of a straightforward displacement by nucleophilic anions.¹²⁵⁾ Halonium ions are detected directly by NMR in $\text{SbF}_5\text{-SO}_2$ at

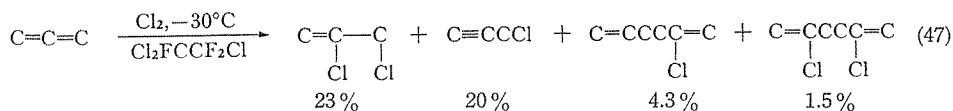
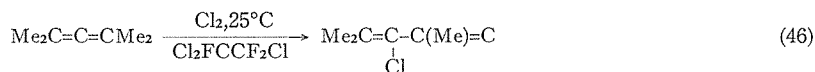
Table 7. NMR Data of Allenyl Halonium Ions (XX) in $\text{SbF}_5\text{-SO}_2$.²⁰⁹⁾



X	H ¹	H ²	CH ²
Cl	9.58	7.07	4.72
Br	9.50	7.28	5.02
I	9.55	7.60	4.77

—80°C.²⁰⁹) A preceding paper for the bromination of 1,2-cyclononadiene, which reported the products consisting of 40% *cis*- and 60% *trans*-2,3-dibromocyclononene,²¹⁰ was disproved by Baird *et al.*, who showed the major product is 1,4-dibromo-*cis*-cyclononene.²¹¹) Caserio *et al.* also obtained 1,4-dibromocyclononene but as a minor product.¹²⁶) The transannular bromination appears to be not general, because the bromination of cycloocta-1,2-diene and cyclododeca-1,2-diene yields only *cis*-2,3-dibromocycloalkenes.²¹²)

When tetramethylallene or 1,1-dimethylallene is treated with chlorine in trichlorotrifluoroethane in the presence of oxygen, a substitution becomes predominant.²¹³)



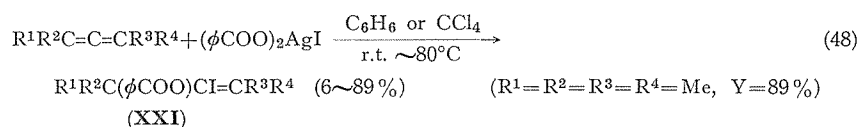
Propadiene also yields the substitution product as well as the addition and dimerization products.²¹³) In the addition of interhalogen compounds or IN_3 to 2,3-pentadiene and cyclononadiene, the attachment of the electrophile to the central carbon of allenic bond and the nucleophile to the terminal one was observed. Generally the *trans* adducts are produced.²¹⁴) Arylsulfonyl or sulfonyl halide reacts with allenes to yield mono adducts having a S-C bonds at the central carbons of allenes in high yields.^{215,216})

The electrophilic addition to 2-methyl-1-(tetramethylcyclopropylidene)propene occurs at the terminal carbon of allenic bond, which is explained by the stability of cyclopropylidene-carbinyl cation. On the other hand, epoxidation and oxymercuration of this allene give central adducts as a result of the product-determining nucleophilic ring-opening of a bridged cation.²¹⁷)

Taylor *et al.* examined the electrophilic and nucleophilic addition reactions for a series of perfluoroallenes.^{218,219}) The site of nucleophilic attack is dependent on the structure of allene owing to the extent of stabilization of negative charge by the β -fluorine atoms.²¹⁹)

In the addition of hypochlorous acid, Cl^+ attacks at the central carbons of allenes and OH^- adds to the more substituted terminal carbons. The yields are fair without accompanying chloroketones.²²⁰)

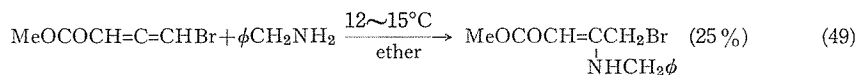
Phenol reacts with allene in the presence of Hg sulfate and sulfuric acid to give 2,2-bis(4-hydroxyphenyl)propane.²²¹) The reaction of Prevost reagent with allene gives the *cis*- and *trans* monoadduct **XXI**²²²) (Eq. (48)).



The addition of allyl Grignard reagent to buta-2,3-diene-1-ol yields a butadiene derivative, 3-methylenehexa-1,5-diene ($\sim 80\%$) and/or an allyl alcohol, hepta-2,6-diene-1-ol, ($1\sim 2\%$) in ether.²²³)

The base-catalyzed addition of carboxylic acid to dimethylallenylsulphonium bromide readily yields a vinyl ester, which is useful as an acylating reagent for alcohols and amines.⁸²⁾

Amines add to an α -keto-substituted allene to give enamines.⁶²⁾



Epoxidation of alkylated allenes was studied by Crandall *et al.* A bisepoxide is obtained by the reaction of 1,1-dimethyl-*t*-butylallene with peracetic acid,³¹¹⁾ but in the reaction of tetramethylallene, the resulting epoxides rearranges completely.²²⁴⁾

IV.2.2 Radical addition

Radical addition of allenes is investigated in detail by using *t*-butylhypochlorite. The products in the reaction with optically active 2,3-pentadiene in ether are the racemic mixture, *cis*- and *trans*-4-chloro-3-*t*-butoxy-2-pentene, and 3,4-dichloro-2-pentene, indicating the intervention of a symmetric resonance-stabilized allylic intermediate. In hydrocarbon solvents, substitution becomes predominant and the product is racemic 4-chloro-2-pentyne formed from the resonance-hybridized 2,3-pentadienyl radical.²²⁵⁾ The hybrid nature of propargylic radical, instead of an equilibrium mixture, is verified by Poutsma by means of chemical technics.²²⁶⁾ The reactivity for the hydrogen abstraction by *t*-BuO radical decreases in the following order, allenic hydrogen \sim propargylic hydrogen $>$ allylic hydrogen,²²⁵⁾ and the relative reactivity coefficients, *k*, for tertiary propargylic hydrogen, allenic hydrogen and allylic hydrogen are 13.5, 4.0, and 1.05, respectively, where cyclopentyl hydrogen is taken as a standard.²²⁶⁾ Similar results are also obtained from an ESR study of the reaction of methylallene with *t*-butoxy radical.¹⁴⁰⁾

In the gas-phase free radical addition of hydrogen bromide to allenes, methyl substituents in the reactant accelerates the reaction rate. The activation energies for the reaction with propadiene, 1,2-butadiene, 3-methyl-1,2-butadiene and 2,3-pentadiene are -3.43 , -3.44 , -4.17 , and -4.06 kcal/mol, respectively.²²⁷⁾ The addition of tetrafluorohydrazine to allene takes place under the influence of light of 2537 Å to give a mixture of 2-fluoro-3-difluoroaminopropene and 3-difluoroaminopropyne in a total 70% yield.²²⁸⁾

IV.2.3 Miscellaneous additions

The addition of carbenes to allenes yields the derivatives of methylenecyclopropane.^{229,230)} Doering *et al.* studied the reaction by using dideuteromethylene and found a random distribution of deuterium in the resulting methylenecyclopropane, which suggests a symmetric intermediate or an excited methylenecyclopropane intermediate.²³¹⁾ In the reaction of phenylallene with dichlorocarbene, only 2-methylene-3-phenyl-1,1-dichlorocyclopropane is obtained.²³⁰⁾

Hydroboration of allene is studied with bisamylborane^{232,233)} or 4,4,6-trimethyl-1,3,2-dioxaborinane.²³⁴⁾ The reaction is affected principally by steric effect. Terminal allene yields the products with the attachment of boron at the unsubstituted terminal carbon, and more substituted allenes tend to give the adducts with the attachment of boron at the central carbon of the allenic bond. Cycloallenes yield the latter products. Electronic effect

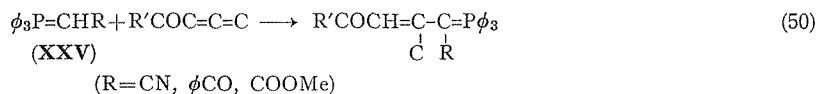
of substituents influences the orientation of these addition reactions only with secondary importance.

Allene undergoes an ene reaction, but it is more or less accompanied by the cycloaddition reaction described in IV.1.2. Photo-generated benzyne reacts with allenes as follows.¹⁷⁷⁾ The ene reaction of alkyl substituted allenes is generally accompanied by

Table 8. Reaction of Benzyne with Allenes.¹⁷⁷⁾

Allene	Products (%)		
	XXII	XXIII	XXIV
Me ₂ C=C=C	34		
MeC=C=CMe	18	30	
C=C=C		16	
C ₆	31	0	5
<i>t</i> -BuC=C=COMe		26	25
<i>t</i> -BuC=C=COEt		26	17
C=C=CCl		1	12
C=C=CCN		15	

rearrangement to yield the butadiene-derivatives of type **XXII**. Especially, tetramethylallene reacts with substituted acetylenes having electron withdrawing groups,²³⁵⁾ acrylonitrile,³⁰⁹⁾ 1, 1, 1-trifluoropropane,²³⁵⁾ trifluoronitrosomethane,²³⁵⁾ bis(trifluoromethyl)ketene,²⁸⁾ EtOCOC=NCOC₂Et,²³⁵⁾ and (*φ*)₂C=S²³⁶⁾ to yield the adducts of type **XXII** in moderate to excellent yields. Bis(trifluoromethyl)ketene reacts at both reaction sites, the carbon-carbon double bond and the carbonyl group.²⁸⁾ Dolbier, Jr. and Dai examined the deuterium isotope effect in the reaction of propadiene with hexafluorocyclobutanone, and found the reaction proceeds by a concerted process.²³⁷⁾ Allenic diphenylphosphineoxides are methylated at the double bond adjacent to phosphorus by lithium dimethyl copper.²³⁸⁾ Electronegative-group-substituted methylenetriphenylphosphoranes (**XXV**) undergo the Michael type addition reaction with allenyl ketones to give new alkylenephosphoranes.²³⁹⁾



IV.3: Homoallenic Participation²⁴⁰⁻²⁵³⁾

The solvolysis rates of β -allenic esters are accelerated more significantly than those of the corresponding olefinic esters (homoallylic participation) and the rearranged products are formed. The participation by allenic bond is called homoallenic participation.²⁴⁰⁾ The ester group in the γ -position of allenic bond also receives such participation but with lesser extent.²⁴⁶⁾

IV.4: Miscellaneous Reaction

Reduction of allenes: Birch reagent reduces alkyl allenes to the *trans* olefins and aryl allenes to the alkyl benzenes.²⁵⁴⁾ On the contrary, cyclic allenes yield mainly the *cis* cyclic olefins, and the *trans* adduct increases for olefins with larger rings.²⁵⁵⁾ Only the *cis* cyclic olefins are formed from C₉ and C₁₀ cyclic allenes and in the case of C₁₄ cyclic allenes, 73% of the products is composed of the *trans* olefin. With diimide, aliphatic or cyclic allenes are reduced at the least substituted double bond, and yield the *cis* olefins with little contamination of the rearranged products or the over-reduced products.²⁵⁶⁾

Table 9. Reduction of Acyclic Allenes by Sodium in Liquid Ammonia.²⁵⁴⁾

Allene	Product	
	Yield (%)	Distribution (%)
1,2-nonadiene	80	<i>trans</i> -2-nonene 92.8
		<i>cis</i> -2-nonene 7.2
2,3-nonadiene	85	<i>trans</i> -2-nonene 49.2
		<i>cis</i> -2-nonene 1.5
		<i>trans</i> -3-nonene 47.9
		<i>cis</i> -3-nonene 1.4
4,5-nonadiene	82	<i>trans</i> -4-nonene 96.6
		<i>cis</i> -4-nonene 3.4
tetramethylallene	76	2,4-dimethyl-2-pentene 100
phenylallene	72	propylbenzene 82
		allylbenzene 18

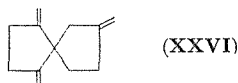
The decomposition or rearrangement of allenes takes place photochemically.^{257,258)} For example, optically active 2,3-pentadiene racemizes at room temperature in the presence of toluene by triplet energy transfer mechanism.²⁵⁹⁾ The thermal decomposition and rearrangement are studied for propadiene²⁶⁰⁾ and 1,2-cyclononadiene.²⁶¹⁾ The rearrangement of 3-alkyl-4-bromo-1,2-butadiene to 3-alkyl-2-bromo-1,3-butadiene occurred also thermally in the presence of a metal salt.^{262,263)}

Allenic halides, unlike vinyl halides, react under the solvolytic conditions.^{61,264-266)} Schiavelli *et al.* examined the solvolysis of triarylchloroallenes. The *m* value for trichloroallene in aqueous acetone is 0.69 ± 0.06 . The activation parameters for triphenylchloroallene are $\Delta H^* = 20.2$ kcal/mol, and $\Delta S^* = -10.7$ e.u. The product in acetone-water is 1,1,3-triphenylprop-2-ynyl-1-ol. The reaction constant ρ against σ^+ is -2.0 . The addition of triethyl amine has no effect on the rate but the addition of LiCl causes a considerable rate depression. They interpreted these results in terms of an S_N1 reaction proceeding *via* a charge-delocalized allenyl cation.^{264,266)}

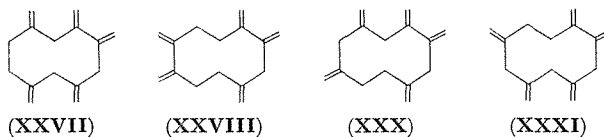
V. TRANSITION METAL CHEMISTRY OF ALLENES**V.1: Transition Metal Catalyzed Reactions of Allenes**

Propadiene oligomerizes in the presence of transition metal compounds such as

rhodium or nickel complexes. With tris(triphenylphosphine)chlororhodium used as a catalyst, a tetramer **XXVI** (55%), a pentamer with unknown structure (16%), and traces of a dimer and a trimer are obtained in chloroform at 70~80°C. The product is accompanied with a little polymer and its formation is accelerated in the presence of acetic acid. Methylacetylene does not react under these conditions. $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ or $\text{Rh}(\text{H}_2\text{C}=\text{CH}_2)_2$ (acac) does not exhibit a satisfactory catalytic effect, and $(\phi_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}$ effectively catalyzes the reaction though an explosion is reported in a large scale

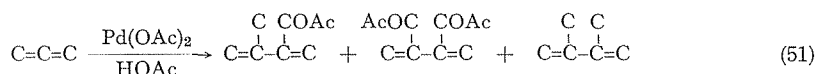


experiment.²⁶⁷⁾ The tetramer **XXVI** is obtained also with a catalyst system of $\text{Rh}_2\text{Cl}_2(\text{CH}_2=\text{CH}_2)_4$ and triphenylphosphine in a 70~80% yield at 60°C. $[\text{RhCl}(\text{CH}_2=\text{CH}_2)\text{P}\phi_3]_2$ reacts similarly with propadiene at room temperature, but $\text{IrCl}(\text{P}\phi_3)_3$ is unreactive.²⁶⁸⁾ In the absence of triphenylphosphine, $\text{Rh}_2\text{Cl}_2(\text{CH}_2=\text{CH}_2)_4$ yields allenepentamer complex, $\text{RhCl}(\text{C}_{15}\text{H}_{20})$, and when carbon monoxide or isonitrile exists instead of triphenylphosphine, a high polymer is produced.²⁶⁸⁾ Bis(cyclooctadiene) nickel yields pentamer **XXVII** selectively (50-55%) at 40~70°C, and another pentamer **XXVIII** is obtained quantitatively by the reaction of rhodium allenepentamer complex, $\text{RhCl}(\text{C}_{15}\text{H}_{20})$, with bisdiphenylphosphinoethane.²⁶⁹⁾ $[\text{p}-(\phi)_2\text{PC}_6\text{H}_4\text{P}(\phi)_2\text{Ni}(\text{CO})_2]_x$ (**XXIX**) catalyzes the oligomerization of propadiene and produces a tetramer **XXVI** and a pentamer, for which the structure **XXX** or **XXXI** is proposed.²⁷⁰⁾



As the catalyst for the trimerization of allenes, nickel carbonyl-triphenylphosphine complexes are well known. Wilke *et al.* has reported that $\text{Ni}(\text{P}(-\text{O}-\text{C}_6\text{H}_4)_3)_2$ catalyzes the conversion of propadiene to 1,2,4-trimethylenecyclohexane.²⁷¹⁾ Here, the formation of the usually accompanying isomer, 1,3,5-trimethylenecyclohexane, is not referred. The complex **XXIX** catalyzes also the gaseous dimerization of propadiene. The catalyzed dimerization yields mainly 1,3-dimethylenecyclobutane, which is a minor product in the thermal dimerization. For example, under the conditions of 200°C, 61% of conversion, and by using He as a diluent, a 60% yield of 1,3-dimethylenecyclobutane and a 12% yield of the 1,2-adduct are obtained.

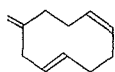
Palladium acetate catalyzes the linear dimerization of propadiene in acetic acid.²⁷²⁾



The catalyst accelerates also the co-dimerization of propadiene with propyne or pentyne.²⁷³⁾

Heimbach *et al.* obtained two 1 : 2 adducts (**XXXII**, **XXXIII**) of propadiene and

butadiene in a maximum 69% yield by using nickel(0)-tris(2-biphenyl) phosphite catalyst.



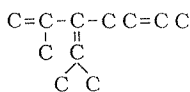
(XXXII)



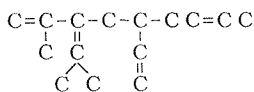
(XXXIII)

XXXII is the major product. Methoxyallene or 1,1-dimethylallene gives similar products. They also obtained bis-(methylene)-twelve-membered-ring compounds consisting of two molecules of butadiene and two of propadiene in 5~13% yields.²⁷⁴⁾

Tetramethylallene reacts with butadiene at 50°C to give linear 1 : 1 and 1 : 2 adducts in an autoclave in the presence of bis(cyclooctadiene)iron, ferric acetylacetonate and triethylaluminium. There are five isomers in the 1 : 1 adducts in which **XXXIVa** is the main component. The 1 : 2 adducts are largely composed of **XXXIVb**. The total yield is 30~50%.²⁷⁵⁾



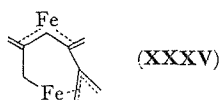
(XXXIV a)



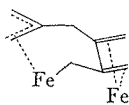
(XXXIV b)

V.2: Transition Metal Complexes

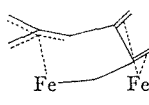
Many allene- and oligoallene-complexes are isolated as the intermediates or the model compounds of the catalytic reactions.²⁷⁶⁻²⁸²⁾ Triirondodecacarbonyl produces three isomeric complexes, **XXXV**, **XXXVI**, and **XXXVII**, in the reaction with propadiene.²⁷⁶⁾



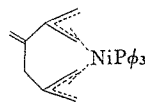
(XXXV)



(XXXVI)



(XXXVII)



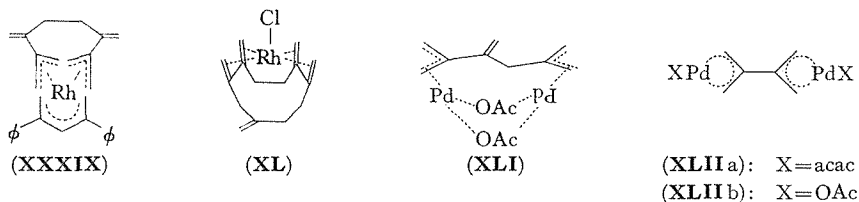
(XXXVIII)

The formation of them, the conversion of **XXXV** to **XXXVI** and **XXXVII**, and the conversion of **XXXVI** to **XXXVII** are the complete intramolecular reactions with no acceleration by light, protic solvents, hydridic reagents, or free-radical reagents. Bis-(cyclooctadiene)nickel reacts with propadiene to yield, after the treatment with triphenylphosphine, a trimer complex, **XXXVIII**, or a tetramer complex, which reacts with CS₂ to yield a cyclic trimer, 1,2,4-trimethylenecyclohexane, or a cyclic tetramer, respectively.²⁷⁷⁾

Bis(ethylene)-1,3-diphenylpropane-1,3-dionatorrhodium and propadiene give a 60% yield of complex **XXXIX** at room temperature,²⁷⁸⁾ and [RhCl(CH₂ = CH₂)₂]₂ yields pentamer complex **XL**.²⁷⁹⁾

Palladium acetate reacts with propadiene to yield a binuclear trimer complex, **XLI**.²⁸⁰⁾

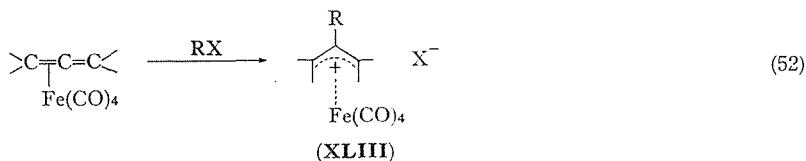
In the reaction of acetylacetonato- π -allylpalladium with propadiene, complex **XLII a** is obtained in a 40% yield besides the insertion product.²⁸¹⁾ The 2,2'-bi- π -allyl ligand is also prepared by the reaction of propadiene with palladium acetate²⁸⁰⁾ or $\text{Fe}_2(\text{CO})_9$.²⁸²⁾



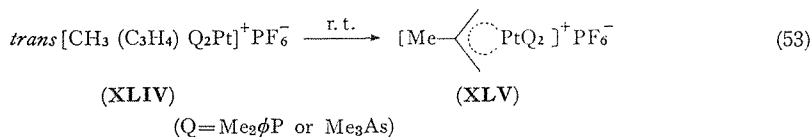
Osborn pointed out that there are two types of coordination of allene on the metal; a monodentate π -co-ordination and a bidentate co-ordination through two σ -bonds.²⁸³⁾ Since then a number of complexes are synthesized such as $\text{Rh}(\text{P}\phi_3)_2\text{Cl}(\text{C}=\text{C}=\text{C}) \cdot 1/2\text{C}_2\text{H}_2\text{Cl}_2$,²⁸³⁾ $\text{RhX}(\text{P}\phi_3)_2(\text{C}=\text{C}=\text{C})$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$),²⁸⁴⁾ $(\text{acac})(\text{tetramethylallene})_2\text{Rh}$,²⁸⁵⁾ $(\text{acac})(1,1\text{-dimethylallene})_2\text{Rh}$,²⁸⁶⁾ $[(1,1\text{-dimethylallene})\text{PtCl}_2]_2$,²⁸⁵⁾ $[(\text{tetramethylallene})\text{Cl}_2\text{Pt}]_2 \cdot 2\text{CCl}_4$,²⁸⁵⁾ $(\text{tetramethylallene})\text{Cl}_2\text{Pt}(\text{NC}_5\text{H}_4\text{-}i\text{-}p\text{-X})$ ($\text{X} = \text{NH}_2, \text{CH}_3, \text{Et}, \text{H}, \text{Br}, \text{or CN}$),²⁸⁷⁾ $(1,1\text{-dimethylallene})\text{Cl}_2\text{Pt}(\text{NC}_5\text{H}_5)$,²⁸⁷⁾ $(\text{acac})_2\text{Rh}_2(\text{CO})_2(\text{C}=\text{C}=\text{C})$,²⁸⁶⁾ and $\text{Pt}(\text{P}\phi_3)_2(\text{C}=\text{C}=\text{C})$.²⁸⁸⁾ With an exception of the last complex, π -co-ordination is generally accepted. But the co-ordinated allenes in these complexes are not linear, which suggests a considerable extent of rehybridization of orbitals.

A (π -1,2-cyclononadiene)dichloroplatinum(II) complex having an optically active amine ligand is used for the resolution of the allene as already described in section I. 5.¹²⁸⁾

The co-ordinated allene in an allene tetracarbonyl iron complex reacts with electrophilic reagents to yield π -allylic cationic complexes (Eq. (52)).

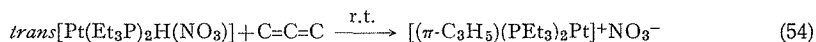


The reaction with hydrogen tetrafluoroborate gives π -allylic complex **XLIII** ($\text{R} = \text{H}$, $\text{X} = \text{BF}_4$) in acetic anhydride, and the reaction with acetyl or benzoyl chloride in the presence of aluminium chloride in dichloromethane yields **XLIII** ($\text{R} = \text{Ac}$ or ϕCO , $\text{X} = \text{AlCl}_4^-$).²⁸⁹⁾ Another allene complex, **XLIV**, undergoes intramolecular rearrangement at ambient temperature to give π -allylic complex **XLV**.²⁹⁰⁾

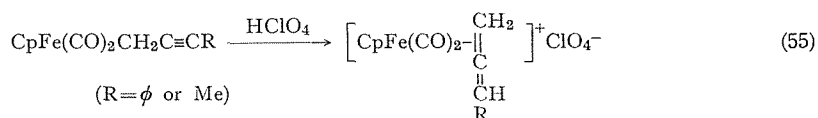


The above reaction seems to be a model reaction for insertion, but the insertion of allene into a π -allylic palladium complex is reported to be not a co-ordination-insertion process but an "actual" insertion step.²⁹¹⁾

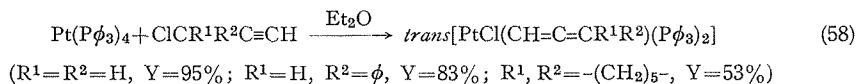
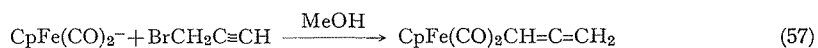
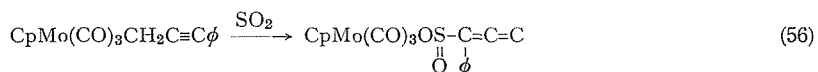
Free propadiene reacts with a hydro-complex to yield a π -allylic complex, which is isolated as hexafluorophosphorous salt or tetraphenylborate²⁹² (Eq. (54)).



Cationic propadiene complexes are prepared also by the protonation of a σ -propargylic complex²⁹³ (Eq. (55)).



A σ -propargylic molybdenum, tungsten, or manganese complex yields another complex having an allenic bond in a ligand in the reaction with sulfur dioxide²⁹⁴ (Eq. (56)). σ -Allenic iron or platinum complexes were prepared by the reaction of propargyl halides with cyclopentadienyldicarbonyliron monoanion (Eq. (57))²⁹⁵ or tetrakis(triphenylphosphine)-platinum^{296,297} (Eq. (58)).



The rate of insertion of propadiene into a π -allyl-palladium bond is increased by the electron attracting substituent in the allyl group as follows, Cl > COOCH₃ >> H > CH₃.²⁹⁷ The solvent effect of the reaction of propadiene with dichlorobisbenzotriplepalladium is examined.³⁰⁴

V.3: Organomercury Chemistry of Allenes

The stereospecificity of oxymercuration of allene is investigated by several workers.²⁹⁸⁻³⁰¹ The adducts resulting from cyclic allenes and mercuric chloride are *cis* for the nine- and ten-membered cyclic allenes, and 66% of the products is *trans* for the eleven-membered cyclic allene.³⁰⁰ For the 14- or 16-membered cyclic allenes, the *trans* adducts are produced.²⁹⁹ They explained these results from the stabilities of planar allylic intermediates. Caserio *et al.* studied the methoxymercuration of optically active 2,3-pentadiene. Although the reaction with mercuric acetate is a stereospecific *trans* addition through a σ -bonded mercurinium ion intermediate,²⁹⁸ both the methoxymercuration by mercuric chloride and the deoxymercuration are nonstereospecific, which suggests that the intermediate bear a close resemblance to the symmetrical allylic ion.³⁰¹

In connection with oxymercuration, the catalytic addition of alcohols or water to 1,2-cyclononadiene was reported.³⁰² Boron trifluoride acts as a co-catalyst, and mercuric salts and alkyl or aryl mercurials as catalysts. The orientation of addition is opposite to

Table 10. Reaction of Ethanol with Optically Active 1,2-Cyclononadiene.³⁰³⁾

Mercury salt	Co-catalyst	Yield of ethoxycyclo-nonene (%)	$[\alpha]_D^{25}$
EtHgOAc	BF ₃	85	15.3
ϕ HgOAc	BF ₃	42	13.6
Hg(OAc) ₂	—		12.4
Hg(OAc) ₂	BF ₃	67	12.6
Hg(ClO ₄) ₂ ·9H ₂ O	BF ₃	82	12.1
HgO	BF ₃	73	11.1
HgSO ₄		72	10.4
Hg(NO ₃) ₂		51	9.9
Hg(NO ₃) ₂	BF ₃	70	9.9
HgCl ₂ ·Hg(OAc) ₂			6.2
HgF ₂	BF ₃		1.4
HgCl ₂			0.1

that of Brønstead acid-catalyzed addition, yielding no ketones or vinyl ethers. The optical purity of ethanol addition to optically active 1,2-cyclononadiene varies with the sort of mercury salt used.³⁰³⁾ These data suggest that the intermediate is an equilibrium mixture of mercurinium ion and allylic carbonium ion, with the least contribution of mercurinium ion for mercuric chloride and the most contribution for ethylmercuric acetate³⁰³⁾ (Table 10).

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