CONVERSION OF HYDROCARBONS INTO BUTADIENE[1]

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I. INTRODUCTION

Production of synthetic rubber is one of the outstanding scientific and industrial achievements in the war effort. U. S. production will be at the rate of over 1,000,000 tons annually toward the end of 1944. This is the result of intense cooperation of chemists and chemical engineers. Butadiene is one of the key hydrocarbons in the synthetic rubber industry. The present study covers the use of hydrocarbons as source material for the production of butadiene and also notes both experimental and theoretical work on the subject. It is hoped that the ideas submitted will be useful in connection with further development of the synthetic rubber industry.

Ostromyslenskiĭ in 1913 expressed the opinion that butadiene is obtainable from any organic compound by thermal treatment alone (118). He supported his statement with a list of twenty-one methods for preparing alkadienes, principally butadiene. Our study to date indicates that over eighty-five distinct organic reactions yield butadiene.

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Many types of organic compounds have been converted into butadiene (31): alkanes, alkenes, alkadienes, alkynes, cyclanes, cyclenes, aromatics, haloalkanes, haloalkenes, halocyclanes, alkanols, alkenols, alkanals, alkenals, hydroxycyclanes, hydroxybenzenes, dialkyl ethers, alkyl alkenyl ethers, dialkenyl ethers, cyclic oxides, alkanoic acids, alkenoic acids, mono-, di-, and tri-esters, alkenyl sulfides, amines, piperidine, and organic ammonium derivatives. Natural and cracked gases, crude oil and its fractions, natural rubber, "butadiene rubber," and coal also yield butadiene upon thermal treatment. Apparently any petroleum or its products can be converted into butadiene (12, 96).

From the scientific standpoint, the optimum conditions for maximum yields of butadiene and underlying reaction mechanisms for some of the foregoing hydrocarbons are attractive fields for research. From the viewpoint of national defense and economy, petroleum and natural gas are logical sources for the production of many types of unsaturated hydrocarbons (44).

Although butadiene is generally taken to be the only C_4H_6 hydrocarbon produced, careful work is expected to show the presence of at least traces of butadiene-1,2, butyne-1, and butyne-2. Butadiene in this study means the 1,3 or conjugated isomer. The isomers of butadiene-1,3, being more reactive, probably polymerize or decompose or are present in such small percentages that they have not been reported. Highly specific tests for small percentages of isomers in samples of butadiene-1,3 are lacking but are nevertheless desirable.

II. Individual Hydrocarbons

A. ALIPHATIC SERIES

1. Alkanes

a. Thermal conversion

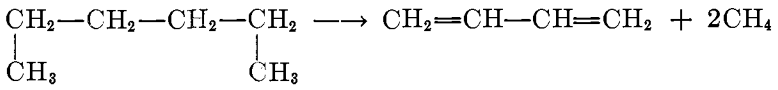
Nine lower alkanes are known to yield butadiene upon thermal treatment at 500–950°C.: methane (63), ethane (64), ethane + propane (17, 163), propane (15, 55, 64), propane + butane (161, 162), propane + butane + pentane (131), *n*-butane (55, 64, 76), 2-methylpropane (76), *n*-pentane (14, 108, 113), 2-methylbutane (14), *n*-hexane (64, 113, 124), and 2-methylpentane (113). The lower-molecular-weight members, e.g., methane, require the highest temperatures. The yields reported in all cases are low, less than 5 per cent on feed per pass, indicating a need of additional experiments to establish guiding principles. Butadiene from hydrocarbons is a reaction product of relatively high temperatures. Its heat of formation is -26 kcal. per gram-mole at 18°C., comparable to -53.9 kcal. for ethyne. Consequently, some of the techniques used in the production of ethyne, such as rapid cooling of reaction products from the electric-arc treatment of hydrocarbons, may be applied in the case of butadiene.

Electric-arc treatment of alkane gases or vapors also yields butadiene, as in the cases of methane (153), and *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane (127). The high temperature of the electric arc relates these conversions to the corresponding thermal treatments. All auxiliary or electrical effects, such as enhanced ionization, polarizations, or radiation, are elusive and may not exist (154).

Theory concerning the thermal decomposition of alkanes may be said to begin with the work of Haber on *n*-hexane (59, 60, 61). He contended that the primary decomposition of *n*-hexane and similar alkanes was scission of the molecule into methane and the complementary alkene. Ostromyslenskiĭ's views were probably greatly influenced by the foregoing study. In explaining the formation of butadiene from alkanes, this experimenter proposed the following equation (124):

$$RC_4H_8R' \rightarrow CH_2{=}CH{-}CH{=}CH_2 + RH + R'H$$

in which R and R′ are alkyl groups. Demethanation of *n*-hexane was given as a specific example:



$$\underset{\displaystyle CH_3}{\underset{|}{CH_2}}{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH_2}} \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + 2CH_4$$

The general process was described as "liberation of RH (R being an alkyl) from straight chain saturated hydrocarbons regardless of their composition and structure." The words "straight chain" should not be taken too literally, because some branched-chain hydrocarbons were included. The statement apparently was intended to exclude cyclic hydrocarbons. Actually, the conversions were regarded as a sequence of two dealkanations (123, 124):

$$RC_4H_8R' \rightarrow RC_4H_7 + R'H$$

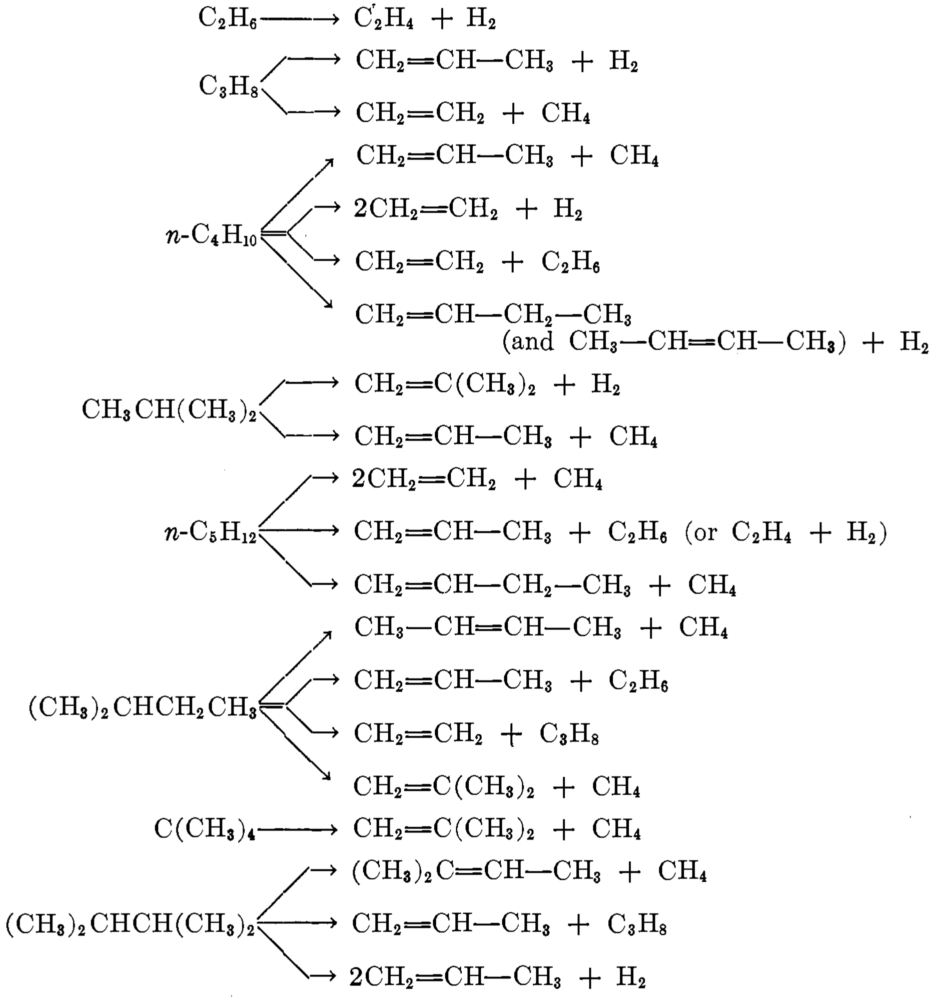
$$RC_4H_7 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + RH$$

Accordingly, thermal degradation of *n*-hexane should give first methane plus pentene-1, and secondly, methane plus butadiene from the pentene.

Any extended explanation of butadiene formation in alkane pyrolysis must consider the rôle of primary decomposition. Hurd, disagreeing with Haber's belief that *n*-hexane first splits into methane and pentene, stated (69): "His data show that the chief unsaturated reaction product is propene and not amylene. Therefore, without proof to the contrary, one may question Haber's assertion that the amylene decomposed at once into propene and ethene. It seems reasonable to infer that propene was formed as a primary product."

Hague and Wheeler observed that dehydrogenation is less important in the decomposition of higher alkanes at lower temperatures (64). Demethanation of propane and *n*-butane exceeded the corresponding dehydrogenations. Also, the deëthanation of *n*-butane was greater than either its demethanation or its dehydrogenation at 650–700°C. These observations have probably influenced subsequent theories to a marked extent. For example, Frey has pointed out (53): "Paraffin hydrocarbons decompose chiefly into simpler complementary olefins and paraffins. High decomposition temperatures favor the concomitant formation of complementary olefins and hydrogen, and in some cases more than two hydrocarbon product molecules are formed. Two reaction mechanisms in accord with these observations have been proposed."

Types of primary decomposition were summarized by Frey as follows:



$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

$$C_3H_8 \longrightarrow CH_2{=}CH{-}CH_3 + H_2$$
$$C_3H_8 \longrightarrow CH_2{=}CH_2 + CH_4$$

$$n\text{-}C_4H_{10} \longrightarrow CH_2{=}CH{-}CH_3 + CH_4$$
$$n\text{-}C_4H_{10} \longrightarrow 2CH_2{=}CH_2 + H_2$$
$$n\text{-}C_4H_{10} \longrightarrow CH_2{=}CH_2 + C_2H_6$$
$$n\text{-}C_4H_{10} \longrightarrow CH_2{=}CH{-}CH_2{-}CH_3 \text{ (and } CH_3{-}CH{=}CH{-}CH_3) + H_2$$

$$CH_3CH(CH_3)_2 \longrightarrow CH_2{=}C(CH_3)_2 + H_2$$
$$CH_3CH(CH_3)_2 \longrightarrow CH_2{=}CH{-}CH_3 + CH_4$$

$$n\text{-}C_5H_{12} \longrightarrow 2CH_2{=}CH_2 + CH_4$$
$$n\text{-}C_5H_{12} \longrightarrow CH_2{=}CH{-}CH_3 + C_2H_6 \text{ (or } C_2H_4 + H_2)$$
$$n\text{-}C_5H_{12} \longrightarrow CH_2{=}CH{-}CH_2{-}CH_3 + CH_4$$

$$(CH_3)_2CHCH_2CH_3 \longrightarrow CH_3{-}CH{=}CH{-}CH_3 + CH_4$$
$$(CH_3)_2CHCH_2CH_3 \longrightarrow CH_2{=}CH{-}CH_3 + C_2H_6$$
$$(CH_3)_2CHCH_2CH_3 \longrightarrow CH_2{=}CH_2 + C_3H_8$$
$$(CH_3)_2CHCH_2CH_3 \longrightarrow CH_2{=}C(CH_3)_2 + CH_4$$

$$C(CH_3)_4 \longrightarrow CH_2{=}C(CH_3)_2 + CH_4$$

$$(CH_3)_2CHCH(CH_3)_2 \longrightarrow (CH_3)_2C{=}CH{-}CH_3 + CH_4$$
$$(CH_3)_2CHCH(CH_3)_2 \longrightarrow CH_2{=}CH{-}CH_3 + C_3H_8$$
$$(CH_3)_2CHCH(CH_3)_2 \longrightarrow 2CH_2{=}CH{-}CH_3 + H_2$$

The rôle of secondary reactions in the formation of butadiene and more conjugated products (aromatics) has been considered by Frolich, Simard, and White (55). These workers suggest the following series of reactions to account for the formation of high-boiling compounds: (*a*) cracking of alkanes into alkenes, (*b*) formation of butadiene from pairs of alkene molecules, (*c*) formation of an aromatic from butadiene and an alkene (18), and (*d*) interaction of aromatics and alkenes to form heavier compounds. Butadiene was considered to be formed from ethene and propene, representing primary reaction products as follows:

$$2C_2H_4 \rightarrow C_4H_6 + H_2$$
$$2C_3H_6 \rightarrow C_4H_6 + C_2H_6$$
$$C_2H_4 + C_3H_6 \rightarrow C_4H_6 + CH_4$$

Frey has also considered the rôle of hydrogen migration in the thermal decomposition of alkanes, including the mechanism of transfer of a hydrogen atom from the carbon atom one removed from the fracture point to the other fragment formed (53). The possibilities include a dissociation into alkyl radicals, one of which acquires a hydrogen atom from the other (68), and a semi-ionization process whereby one radical may transfer its allegiance to the hydrogen atom of the other radical (13). Kassel has suggested that the decomposition may involve formation of alkane and alkylidene, the latter rearranging to alkene (85), or formation of three molecules without the formation of free alkyl radicals (86). For example, *n*-butane would form one hydrogen and two ethene molecules if two hydrogen atoms at opposite ends of the carbon chain come into proximity. *n*-Pentane would yield methane instead of hydrogen.

Schmidt has formulated a double-bond rule, maintaining that the double bond between two carbon atoms strengthens the adjacent single bonds and weakens the next following (139). The mechanism of bond scission was later considered from the electronic standpoint (140). Cracking of alkanes was explained in the following way (140):

> "The first reaction is the formation of a double bond by the splitting-off of two hydrogen atoms. The location of the double bond is then decisive for the location of rupture. This hypothesis is not the customary one. Heretofore it has been assumed that the breaking of a bond between two carbon atoms is the first step in the cracking reaction. . . .
>
> "In cracking aliphatic hydrocarbons, the scission in which chains of three carbon atoms are formed is favored (139). Using the double bond rule, we assume that the first step of the cracking process is the formation of a double bond in position 1:2, by splitting off two hydrogen atoms in the same position and find:

$$\begin{array}{l}
CH_3—CH_2—CH_2—CH_2—CH_2—CH_3 \rightarrow CH_2{=}CH—CH_2—CH_2—CH_2—CH_3 + H_2.\text{"} \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_2{=}CH—CH_3 + CH_3—CH_2—CH_3
\end{array}$$

Staudinger, however, antedates Schmidt in pointing out the weakness of β-bonds in general, e.g., alkyl compounds and grouping were extensively considered (146, 147, 149, 150).

Since *n*-hexane produces butadiene upon thermal treatment at 500–900°C. (64, 113, 124), Schmidt's explanation must be amended. The production of butadiene can be ascribed either to scission of hexene-2 or to conversion of propane and/or propene. The former appears more probable:

$$CH_3—CH{=}CH—CH_2—CH_2—CH_3 \rightarrow CH_3—CH{=}CH—CH_3 + CH_2{=}CH_2$$

or

$$\begin{array}{r}
CH_3—CH{=}CH—CH_2—CH_2—CH_3 + H_2 \rightarrow CH_3—CH{=}CH—CH_3 \\
+ CH_3—CH_3
\end{array}$$

Dehydrogenation of butene-2 would then produce butadiene.

Kassel stated that it appears possible to give a nearly complete account of the decomposition reactions of organic chemistry in terms of 1,1, 1,2, and 1,4 unsaturation (86). Referring to the usual 1,4 reactions involving a system of conjugated double bonds between carbon atoms and with retrospect to the views (49) of Eyring, Sherman, and Kimball on the addition of hydrogen or bromine to butadiene, Kassel writes:

> "There is also a second possible type of 1:4 dehydrogenation:
>
> $$CH_3CH_2CH_2CH_3 \rightarrow H_2 + CH_2{=}CH_2 + CH_2{=}CH_2$$
>
> This type actually corresponds somewhat more closely to the six-electron model than does the production of butadiene from butylene. It is approximately 20 kcal. more endothermic, however, since it takes more energy to break C—C than it does to reduce C═C to C—C. The difference in activation energy will be considerably less than 20 kcal.; accurate predictions are impossible, but it appears worth while to look for this type of decomposition of hydrocarbons with a straight chain of at least four carbon atoms. By analogy with the 1:2 case, we shall expect to find 1:4 loss of methane, ethane, etc."

Referring back to Frey's types of primary decomposition for alkanes and taking into account the established thermal dehydrogenations (7, 14, 51, 107, 111, 155, 158) of butene-1, *cis*-butene-2, and *trans*-butene-2 into butadiene, the last hydrocarbon may be a secondary product from such alkanes as *n*-butane, *n*-pentane, and 2-methylbutane. Thermal condensation of ethene (52, 63, 110, 114, 138, 142, 144, 155, 157, 158, 164) also yields butadiene, so that the latter could be a secondary or tertiary product from ethane, propane, *n*-butane, *n*-pentane, and 2-methylbutane. Whenever ethene dehydrogenates to vinyl radicals and then condenses, butadiene is a secondary product. But the polymerization of ethene into a straight-chain butene, followed by the latter's dehydrogenation, gives the same diene as a tertiary product from the alkane (ethane, propane, *n*-butane, 2-methylpropane, *n*-pentane, and 2-methylbutane). Finally, in order to obtain butadiene from 2-methylpropene, i.e., as a tertiary product in the "decomposition" of 2-methylpropane, 2-methylbutane, or tetramethylmethane, it is necessary to isomerize the branched alkene into butene-1 or butene-2.

A theoretical approach not entirely different from the discussion on the rôle of primary decomposition is the *a priori* view afforded by a "new" theory. To keep the discussion in accordance with the writings of chemical physicists, we shall first consider the nomenclature of intact groups and isolated radicals, leaving all distinctions between groups and radicals to the text or reader. Organic nomenclature begins logically with the names of the large classes of hydrocarbons: namely, the alkanes, alkenes, alkadienes, alkynes, alkenynes, alkadiynes, cyclanes, cyclenes, bicyclanes, bicyclenes, and aromatics. Monovalent groups and radicals, which are formed respectively by replacement or loss of a hydrogen atom, are known generically as alkyl, alkenyl, alkadienyl, alkynyl, alkenynyl, alkadiynyl, cyclanyl, cyclenyl, bicyclanyl, bicyclenyl, or aryl groups and radicals. The names of specific groups and radicals retain the roots of individual hydrocarbon names, as shown in table 1. Divalent groups and radicals are named as diyls; poly-yls are encountered also.

In the case of specific groups and radicals, it is customary to assign definite

TABLE 1

Nomenclature of groups and radicals

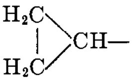
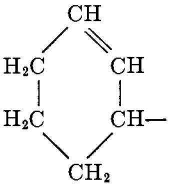
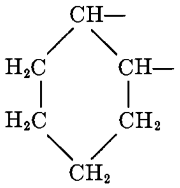
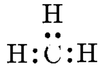
RADICAL	NAME
Monovalent:	
$\underset{\vert}{C}H_2CH_2CH_2CH_3$	Butyl-1
$CH_3\underset{\vert}{C}HCH_2CH_3$	Butyl-2
$\underset{\vert}{C}H{=}CHCH_2CH_3$	But-1-en-1-yl
$CH_2{=}\underset{\vert}{C}CH_2CH_3$	But-1-en-2-yl
$CH_2{=}CH\underset{\vert}{C}HCH_3$	But-1-en-3-yl
$CH_2{=}CHCH_2\underset{\vert}{C}H_2$	But-1-en-4-yl
$\underset{\vert}{C}H_2CH{=}CHCH_3$	But-2-en-1-yl
$CH_3\underset{\vert}{C}{=}CHCH_3$	But-2-en-2-yl
$\underset{\vert}{C}H{=}CHCH{=}CH_2$	Buta-1,3-dien-1-yl
$\underset{\vert}{C}H_2C{\equiv}CCH_3$	But-2-yn-1-yl
$CH{\equiv}CCH{=}\underset{\vert}{C}H$	But-3-en-1-yn-4-yl
$\underset{\vert}{C}{\equiv}CC{\equiv}CH$	Buta-1,3-diyn-1-yl
	Cyclopropyl
	Cyclohex-1-en-3-yl
Divalent:	
$-\underset{\vert}{C}HCH_3$	Ethane-1,1-diyl
$\underset{\vert}{C}H_2\underset{\vert}{C}H_2$	Ethane-1,2-diyl

TABLE 1—*Continued*

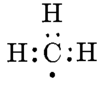
RADICAL	NAME
$\underset{\mid}{CH_2}CH_2\underset{\mid}{CH}CH_3$	Butane-1,3-diyl
$\underset{\mid}{CH}{=}\underset{\mid}{CH}$	Ethene-1,2-diyl
$\underset{\mid}{CH}{=}CHCH_2\underset{\mid}{CH_2}$	But-1-ene-1,4-diyl
$CH_2{=}CH\underset{\mid}{CH}\underset{\mid}{CH_2}$	But-1-ene-3,4-diyl
$\underset{\mid}{CH_2}\underset{\mid}{C}{=}CHCH_3$	But-2-ene-1,2-diyl
$\underset{\mid}{CH_2}CH{=}CH\underset{\mid}{CH_2}$	But-2-ene-1,4-diyl
$\underset{\mid}{CH}{=}\underset{\mid}{C}CH{=}CH_2$	Buta-1,3-diene-1,2-diyl
$\underset{\mid}{CH}{=}CHCH{=}\underset{\mid}{CH}$	Buta-1,3-diene-1,4-diyl
	Cyclohexane-1,2-diyl
Polyvalent:	
$\underset{\mid}{CH_2}\underset{\mid}{CH}\underset{\mid}{CH}CH_3$	Butane-1,2,3-triyl
$\underset{\mid}{CH_2}\underset{\mid}{CH}\underset{\mid}{CH}CH_2CH_3$	Pentane-1,2,3-triyl
$-\underset{\mid}{CH}\underset{\mid}{CH}-$	Ethane-1,1,2,2-tetrayl
$-\underset{\mid}{CH}\underset{\mid}{CH}CH_2\underset{\mid}{CH_2}$	Butane-1,1,2,4-tetrayl
$-\overset{\mid}{\underset{\mid}{C}}-\overset{\mid}{\underset{\mid}{C}}-$	Ethanehexayl

electrical charges to the carbon atoms whose valencies are "exposed." Such carbon atoms are positive, neutral, or negative, according to whether they expose zero, one, or two electrons. The corresponding radicals are known as positive ions, free radicals, and negative ions, respectively. Three kinds of methyl radicals, for example, could be considered:



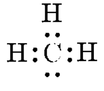
$$\begin{array}{c}\mathrm{H}\\ \cdot\cdot\\ \mathrm{H:\!C\!:H}\end{array}$$

Positive ion



$$\begin{array}{c}\mathrm{H}\\ \cdot\cdot\\ \mathrm{H:\!C\!:H}\\ \cdot\end{array}$$

Free radical

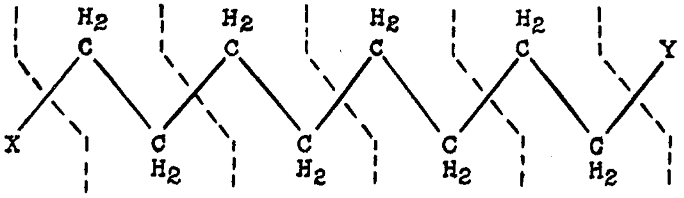


$$\begin{array}{c}\mathrm{H}\\ \cdot\cdot\\ \mathrm{H:\!C\!:H}\\ \cdot\cdot\end{array}$$

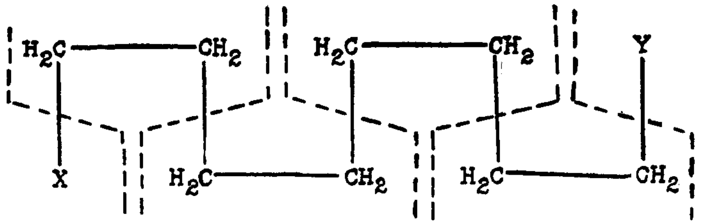
Negative ion

When a solid line instead of a designated number of electrons is used in structural formulas of radicals, it remains to be decided which of the three types of radicals is most probably present.

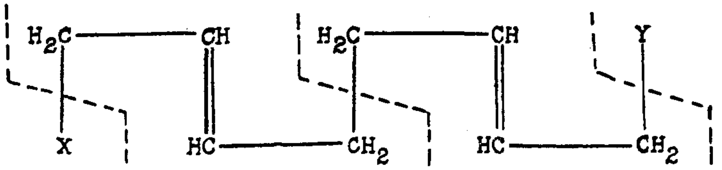
In the thermal treatment of hydrocarbons, including alkanes, alkenes, alkynes, and cyclanes, ethane is a reaction product (25, 46). Its formation can be taken as an indication of the presence of successive units of two carbon atoms in many hydrocarbons. The formation of ethyne can often be explained on the same basis. The basic cause of the aforesaid formation of ethene, ethyne, and butadiene in the thermal conversions of higher alkanes and alkenes or those containing more than four consecutive methylene groups is an inherent deficiency in alternate carbon–carbon bond strengths. Points of scission corresponding to weakness in bonds will be indicated by segmented lines, as in the following formula for a higher alkane:



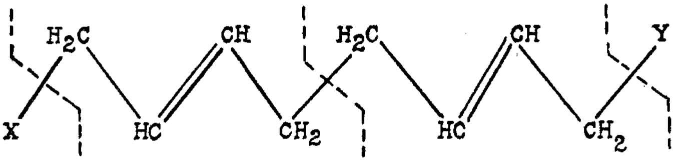
We ascribe such deficiency in bond strengths mainly to shearing forces caused by the repulsion of hydrogen atoms facing each other, especially in *cis* structures:



Cis structures are probably formed whenever the aforesaid molecules are subjected to high rates of energy input under high-temperature conditions. Mixed *cis* and *trans* structures, of course, would prevail in the interim. In the two molecules depicted, X and Y represent inactive groups. They enclose an active chain of ethanediyls about to form ethene fragments ("C_2H_4 directive fragmentation"). The conditions under which fragments of butene, hexene, etc. are directly formed do not need to be considered now. The weak C—C bonds presumably would vie with the adjacent C—H bonds for additional attractive strength. Consequently, thermal dehydrogenation would center about initially weak C—C bonds and would there be competitive with chain scission. Double bonds formed by dehydrogenation would strengthen the linkage between all pairs of carbon atoms that lose hydrogen and would correspondingly further weaken the C—C bonds in the β-position so that scissions would occur:



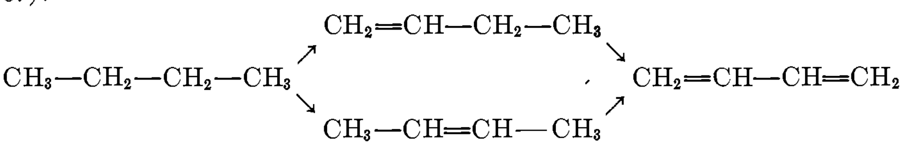
Inspection of Fisher–Hirschfelder atom models indicates that the corresponding *trans* molecules would undergo scission also:



We shall call the over-all process a "C_4H_8 directive fragmentation."

b. Catalytic conversion

Alkanes may be converted in other ways than thermal treatment *per se.* Dehydrogenation of *n*-butane into butadiene can be conducted catalytically in several ways: one-stage catalysis (400–650°C.) and two-stage catalysis (482–650°C.). One-stage catalysis is a process requiring reduced pressure and short contact time (91). By a single passage, 12.2 weight per cent of butane was converted into butadiene with less than 0.2 per cent by weight of carbon. On recycling, 74 weight per cent of butadiene may be produced with the deposition of 2.3 weight per cent of carbon on the catalyst. The catalyst may be chromia (54) or else alumina supporting some chromia, molybdenum trioxide, or vanadium trioxide (58). Two-stage catalysis first forms butene-1 and butene-2, which are dehydrogenated in the second stage under subatmospheric pressure (79, 145, 156, 167):

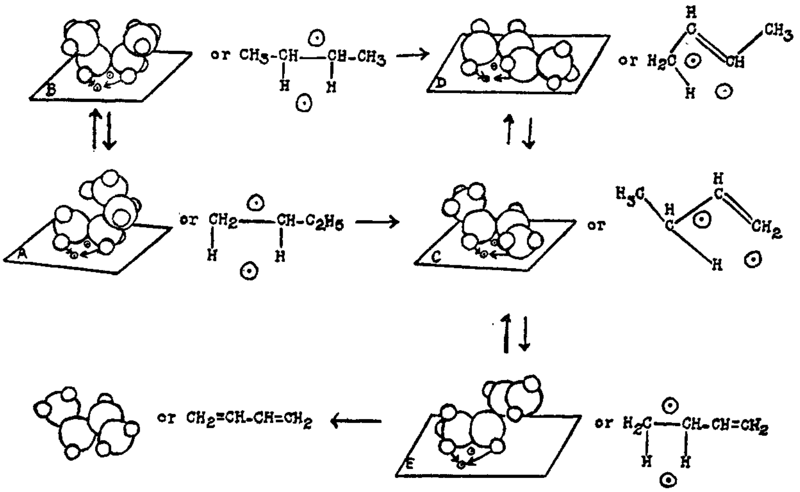


$$\begin{array}{ccccc} & \nearrow & CH_2{=}CH{-}CH_2{-}CH_3 & \searrow & \\ CH_3{-}CH_2{-}CH_2{-}CH_3 & & & & CH_2{=}CH{-}CH{=}CH_2 \\ & \searrow & CH_3{-}CH{=}CH{-}CH_3 & \nearrow & \end{array}$$

Butadiene yields up to 67 per cent by weight of *n*-butane charge are obtainable in the recycling operation. It is desirable that the butenes entering the second stage be devoid of hydrogen and of unreacted *n*-butane. This facilitates the final dehydrogenation to butadiene. A catalyst is generally used in both stages.

In one butadiene process, heat generated during the regeneration of carbonized catalyst is utilized in the dehydrogenations. A heat balance is secured by adjusting the prevailing pressures (1, 2, 116). Pyrolysis at 680°C. over porcelain balls or quartz pieces in the presence of carbon dioxide can be employed alternatively in the second stage (79). The carbon dioxide atmosphere serves to decrease the partial pressure of the butenes and may possibly oxidize some of the hydrogen to water.

Balandin believes that an edgewise orientation of *n*-butane molecules about the active centers (atoms) of a chromia catalyst leads to formation of butene-1 and butene-2, followed by their interisomerization and only concluded by conversion of butene-1 into butadiene molecules (3). The several steps can be depicted as follows, using Balandin's models:



The upper two rows of structures represent conversions of *n*-butane (*cis* form oriented 1,2 or 2,3 as in A or B) into butene-1 (C) and butene-2 (D) on the surface of the catalyst. Active centers are designated by circles with dots. The parts of the molecule that do not enter into the catalysis are turned away from the catalyst. It will be observed in A, B, and also in E, which is a 3,4 orientation of butene-1, that an atom of the catalyst lies midway between two adjacent carbon atoms (large spheres) each of which loses a hydrogen atom (small sphere) before leaving the surface. Structures C and D represent 1,3 orientations of butene-1 and butene-2, respectively; these forms enable an allylic type of hydrogen migration (isomerization) to occur reversibly. This seems to be important, since it is maintained by Balandin that only butene-1, oriented as in E, can yield butadiene. Unfortunately, the spheres are poor representations of molecular systems comprising nuclei each separated by relatively great distances (8). However, the tetrahedral arrangement of valences is acceptable. The conflict with Schmidt's double-bond rule, whereby butene-1 should give propene plus methylene (eventually ethene), can be overcome by assuming that corresponding "dislocating influences" are absent whenever the carbon atoms of the double bond orient themselves on active centers. Also, the lower temperatures used in catalytic dehydrogenation tend to make the reaction more specific: there is much less dependence on thermal activation of the molecule.

"Catalytic cracking" of 2-methylbutane over silica gel at 680°C. gave butadiene as a product (102a). The conversion temperature was 80°C. higher than that used for the thermolysis (14). Consequently, in the absence of comparable kinetic data, the catalytic activity of silica gel for demethanation plus dehydrogenation may be questioned. The substance may function largely as a heat transfer medium and to some extent as an aromatization catalyst.

2. Alkenes

A variety of reactions are available for the direct conversion of ethene into butadiene: namely, thermal treatment (33), electrical condensation in the presence or absence of ethyne (35), catalytic dehydrogenation over copper (37), partial oxidation in the presence of air, sulfur, ferric oxide, or ferric chloride (36, 37), and condensation with ethanediol-1,2 or ethyne (37). Thermal treatment has been extended to propene, butene-1, butene-2, 2-methylpropene, pentene-1, pentene-2, 3-methylbutene-1, 2-methylbutene-2, hexene-1, 3-methylpentene-1, 4-methylpentene-1, 2,4,4-trimethylpentene, and *n*-hexadecene (33). Catalytic dehydrogenation has been extensively applied to butene-1, butene-2, and their mixtures (36). A small amount of butadiene is formed in the catalytic cracking of butene-1 and butene-2 (45).

a. Ethene

The thermal conversion mechanism for ethene was summarized by Lurie as follows (101):

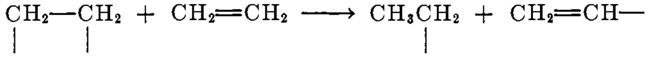
> "It may be assumed that butene is first formed and this is dehydrogenated to butadiene. A different explanation consists in dehydrogenation of ethene to a vinyl radical which condenses with ethene, and the resulting radical is further dehydrogenated to butadiene. Experience shows that simpler conditions are required and higher yields of butadiene obtained when the process is carried out in two stages: at 250–300°, ethene is dimerized and this is followed by dehydrogenation of butene."

Dunstan, Hague, and Wheeler are exponents of a polymerization–dehydrogenation theory (23, 24, 65). They maintain that ethene polymerizes to butene and then dehydrogenates into butadiene (24).

The "different" explanation mentioned in Lurie's review is covered by that of Hurd (70):

> "The bivalent radical from ethylene (listed below as $\underset{|}{CH_2}—\underset{|}{CH_2}$) may be expected to do two things as it comes in contact with unchanged ethylene molecules. It may appropriate hydrogen, a reaction leading to ethane and acetylene, or it may add to the double bond:

Reaction 1.



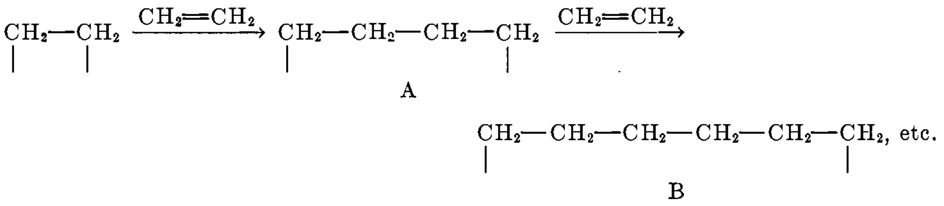
$$\underset{|}{\mathrm{CH_2}}\!-\!\underset{|}{\mathrm{CH_2}} + \mathrm{CH_2{=}CH_2} \longrightarrow \mathrm{CH_3}\underset{|}{\mathrm{CH_2}} + \mathrm{CH_2{=}CH}-$$

or

$$\underset{|}{\mathrm{CH_2}}\!-\!\underset{|}{\mathrm{CH_2}} + 2\mathrm{CH_2{=}CH_2} \longrightarrow \mathrm{CH_3CH_3} + 2\mathrm{CH_2{=}CH}-$$

"The addition reaction may be considered to have the following sequence:

Reaction 2.



$$\underset{|}{\mathrm{CH_2}}\!-\!\underset{|}{\mathrm{CH_2}} \xrightarrow{\mathrm{CH_2{=}CH_2}} \underset{\text{A}}{\underset{|}{\mathrm{CH_2}}\!-\!\mathrm{CH_2}\!-\!\mathrm{CH_2}\!-\!\underset{|}{\mathrm{CH_2}}} \xrightarrow{\mathrm{CH_2{=}CH_2}} \underset{\text{B}}{\underset{|}{\mathrm{CH_2}}\!-\!\mathrm{CH_2}\!-\!\mathrm{CH_2}\!-\!\mathrm{CH_2}\!-\!\mathrm{CH_2}\!-\!\underset{|}{\mathrm{CH_2}}}, \text{ etc.}$$

"Reaction 1 calls for higher temperatures than reaction 2. The univalent radical of (1) may add also to ethylene as in (2), but at their high temperature of formation it is to be expected that the greater part of the $\mathrm{CH_3CH_2}$— and $\mathrm{CH_2{=}CH}$— radicals would change into C_2H_4 and C_2H_2, respectively, by detachment of a hydrogen atom. Some ethane would escape, but much of it would pyrolyze further into $2\mathrm{CH_3}$—, thence into $2\mathrm{CH_4}$ as in reaction 1 or into $2\mathrm{CH_3CH_2CH_2}$—, etc., as in reaction 2. The product (2B) may isomerize to cyclohexane. Dehydrogenation of (A) and (B) would be brought about by collision with other radicals. Thus, (A) would give rise to butadiene and (B) to cyclohexene or benzene. The lower the temperature, the greater should be the tendency for a long polymeric chain."

Zanetti, Suydam, Jr., and Offner stated (164): "The direct formation of butadiene from ethylene takes place according to the equation, $2C_2H_4 \rightarrow \mathrm{CH_2{=}CH{-}CH{=}CH_2} + H_2$. It will be noted that there is no change of volume in this reaction, which means that the pressure in the reactor would have no influence on the quantity of butadiene formed."

Schneider and Frolich rejected the idea that butene is an intermediate in butadiene formation, because data extrapolated for zero per cent cracking showed about 41, 36, 12, and 3 moles of hydrogen, butadiene, propene, and butene, respectively, for each 100 moles of ethene reacting (142). Accordingly, about 72 per cent of the ethene reacting was considered to form butadiene plus hydrogen as initial products:

$$2C_2H_4 \rightarrow C_4H_6 + H_2$$

The following conclusions were part of those made in regard to the thermal cracking at 725°C. of propane, ethene, and propene:

"That cracking reactions are approximately first order and homogeneous is confirmed, even in those cases where the initial products formed point toward a dimolecular reaction. If anything, the order is even lower than first. Thus, while the initial products from both ethylene and propylene indicate that the main reactions are dimolecular, the amount of propylene reacting is actually increased threefold by lowering the concentration of the olefin from one to one-eighth atmosphere by dilution with an inert gas. Also in cracking ethylene, where the main reaction is polymerization of two molecules with simultaneous elimination of hydrogen to form butadiene, it was found necessary to raise the temperature more than 25° in order to obtain the same percentage cracking at atmospheric pressure as that obtained at one-fifth atmosphere. In other words, instead of varying as the square of the pressure (as a simple dimolecular reaction should), the rate increased even less than the first power of the pressure. The absence of surface catalytic effects was shown by packing the cracking tube with broken quartz. As a matter of fact, the results indicate less cracking in a packed tube than in an open one.

"It has been established that higher hydrocarbons can be built up from lower ones otherwise than by simple polymerization. Examination of the initial products from the cracking of ethylene and propylene has shown the importance, not generally recognized hitherto, of reactions of the type,

$$2C_3H_6 \rightarrow C_2H_4 + C_4H_8$$

Other reactions of this type which have been shown to take place are:

$$2C_2H_4 \rightarrow C_4H_6 + H_2$$
$$2C_3H_6 \rightarrow C_2H_6 + C_4H_6$$
$$C_2H_4 + C_4H_6 \rightarrow C_6H_8 + H_2$$
$$C_2H_4 + C_4H_6 \rightarrow C_6H_6 + 2H_2$$

And still others indicated but not definitely proved are:

$$2C_3H_8 \rightarrow C_2H_6 + C_4H_{10}$$
$$2C_3H_6 \rightarrow C_6H_{10} + H_2$$
$$2C_3H_6 \rightarrow C_5H_8 + CH_4$$

"Reactions of this type may be explained satisfactorily on assumption that free radicals exist. Thus,

$$C_2H_4 \rightarrow (CH_2) + (CH_2); \quad (CH_2) + C_2H_4 \rightarrow C_3H_6$$

In the absence of any definite proof, however, it is largely a matter of choice whether one prefers to explain the mechanism on the basis of free radicals or activated molecules.

"That butylene is a probable intermediate in the formation of butadiene, as has recently been stated in the literature (64), is disproved. In the cracking of propylene, there is produced about five times as much butylene as butadiene; in the cracking of ethylene, butadiene is formed in quantities about fourteen times as large as butylene. This would be inconsistent if butadiene were formed by the intermediate production of butylene. Also the method of plotting the results, as explained in the foregoing [extrapolating back to zero per cent cracking], would clearly show butadiene as a secondary product if it were formed through an intermediate as stable as butylene."

The foregoing conclusions have been questioned (28) as follows:

"The conclusion that the formation of butadiene and hydrogen is the immediate result of collision between two ethylene molecules is not justified by the data. The experimenters found it necessary to raise the temperature more than 25° to obtain the same percentage decomposition at 1.0 atmosphere as at 0.2 atmosphere. Instead of varying as the square of the pressure, which would be expected in the case of a second order reaction, the rate increased even less than the first power of the pressure. Apparently, then, the largest proportion of the substances claimed to be initial products could not readily be formed from ethylene without a bimolecular process; yet the decomposition of ethylene follows a course which is more nearly unimolecular than bimolecular. One way of correlating these observations would be to assume that the substances claimed to be initial products are rather the initial stable products which arise, in part at least, from unstable primary decomposition products of ethylene. The extrapolation method of determining primary products would not show such an effect, as may be seen when this method is applied to the decomposition of isobutene at 700°. The curve indicated ethylene as a primary product, which is apparently impossible since the formation of ethylene from isobutene involves the rupture of two separate bonds. The probable explanation, suggested by Hurd (72), is that propylene, one of the primary products, decomposes to form ethylene. Acetylene, produced by dehydrogenation, would be a primary product involving the necessary first order reaction. When the concentration of ethylene is high, i.e., when the decomposition is not extensive, the probable sequel to acetylene formation would be reaction between ethylene and acetylene to form butadiene, a bimolecular process. If the first order reaction producing acetylene is more rapid than the secondary reaction in which it is consumed, it becomes understandable how a decomposition that appears to be of less than second order results in the formation of products which require a bimolecular mechanism. The assumption in this case is that acetylene is produced in considerable quantities and reacts with ethylene almost as rapidly as ethylene dehydrogenates to acetylene, although no direct data are available on this point."

The present authors adopt a non-polymerization view of the main course of ethene conversion, regarding the initial step as an endothermic formation of atomic hydrogen and vinyl radicals:

$$CH_2{=}CH_2 \rightarrow \dot{H} + CH_2{=}\dot{C}H$$

Union of vinyl radicals, which is an exothermic process, would give butadiene, presumably the *trans* form, as the product of a second step:

$$2CH_2{=}\dot{C}H \rightarrow CH_2{=}CH{-}CH{=}CH_2$$

The endothermicity of the first step is much greater than the exothermicity of the second, based on equivalent amounts of vinyl radicals, so that additional exothermic processes of local character become operative at the time vinyl radicals are formed. Such additional steps include: (*a*) association of atomic hydrogens to give molecules, (*b*) union of atomic hydrogens with stray vinyl radicals to re-form ethene molecules, (*c*) partial hydrogenation of ethene by atomic hydrogen, yielding ethyl radicals, (*d*) union of ethyls with atomic hydrogen, developing ethane, (*e*) coupling of ethyl radicals to give *n*-butane, (*f*) addition of ethyl and stray vinyl radicals to form butene-1, and (*g*) polymerization (46) of ethene, producing butene-1 and higher polymers. Steps c and d are additive, as are c plus e:

$$\begin{array}{l} CH_2{=}CH_2 + \dot{H} \longrightarrow CH_3{-}\dot{C}H_2 + E_1 \\ CH_3{-}\dot{C}H_2 + \dot{H} \longrightarrow CH_3{-}CH_3 + E_2 \\ \hline CH_2{=}CH_2 + 2\dot{H} \longrightarrow CH_3{-}CH_3 + E_1 + E_2 \end{array}$$

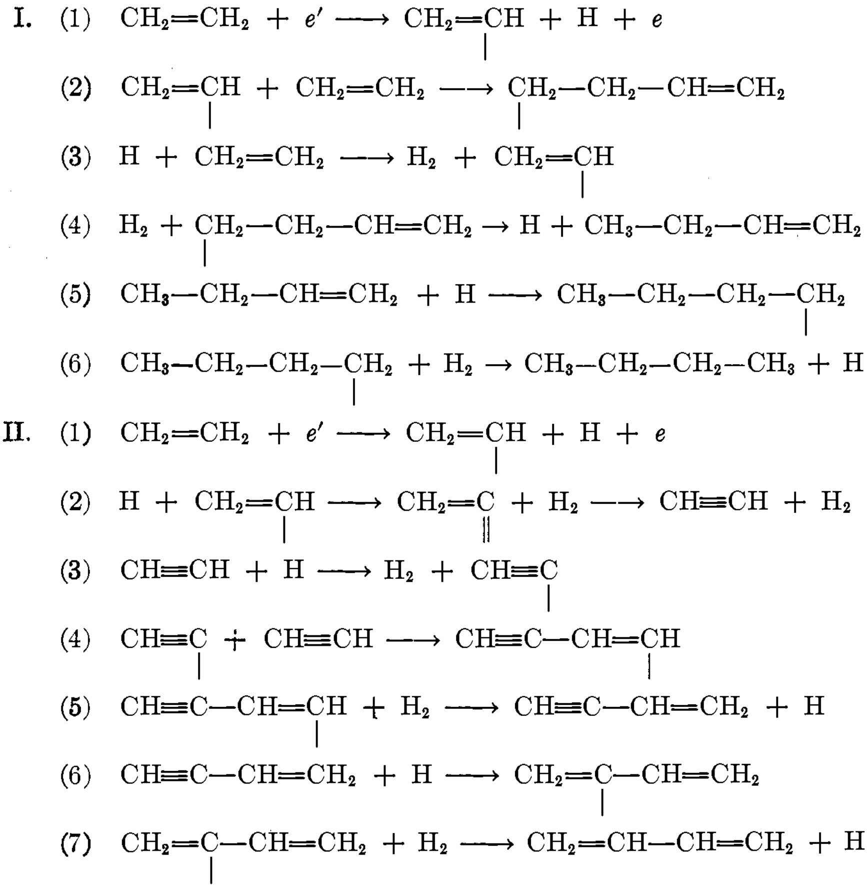
$$\begin{array}{l} 2CH_2{=}CH_2 + 2\dot{H} \longrightarrow 2CH_3{-}\dot{C}H_2 + 2E_1 \\ 2CH_3{-}\dot{C}H_2 \longrightarrow CH_3{-}CH_2{-}CH_2{-}CH_3 + E_3 \\ \hline 2CH_2{=}CH_2 + 2\dot{H} \longrightarrow CH_3{-}CH_2{-}CH_2{-}CH_3 + 2E_1 + E_3 \end{array}$$

The order of increasing exothermicity per two hydrogen atoms or one molecule of butadiene is probably $E_1 + E_2$, $2E_1 + E_3$, whereby the following over-all reaction is predictable for an ideal conversion:

$$4CH_2{=}CH_2 \rightarrow CH_3{-}CH_2{-}CH_2{-}CH_3 + CH_2{=}CH{-}CH{=}CH_2$$

Side reactions would divert much of the *n*-butane into scission products, including additional butadiene.

Favorable to the vinyl interpretation is the fact that the optimum temperature point for the non-catalytic production of butadiene from ethene is above 600°C., considerably higher than the temperature for maximum true polymerization of ethene (27). The investigated temperature range for the conversion of ethene into butadiene is 600–1100°C., but corresponding pressures are not fixed in value (33). An optimum temperature point of 750°C. is reported by one group of workers, who obtained 0.93 weight per cent of butadiene from ethene (164). Other data indicate that 650°C., at which a 4.5 weight per cent yield was obtained, is better than higher temperatures (158). High ethene conversions were obtained at 776°, 848°, and 884°C. by decreasing the contact time with each increase in temperature (144). A maximum butadiene yield of 7.3 weight per cent per pass was obtained. Large amounts of butane and butadiene result when ethene is subjected to a high-frequency discharge (4, 5). The investigators of the last reaction proposed three types of chain reactions to explain the formation of the foregoing products:



I. (1) $CH_2{=}CH_2 + e' \longrightarrow CH_2{=}\underset{|}{CH} + H + e$

(2) $CH_2{=}\underset{|}{CH} + CH_2{=}CH_2 \longrightarrow \underset{|}{CH_2}{-}CH_2{-}CH{=}CH_2$

(3) $H + CH_2{=}CH_2 \longrightarrow H_2 + CH_2{=}\underset{|}{CH}$

(4) $H_2 + \underset{|}{CH_2}{-}CH_2{-}CH{=}CH_2 \rightarrow H + CH_3{-}CH_2{-}CH{=}CH_2$

(5) $CH_3{-}CH_2{-}CH{=}CH_2 + H \longrightarrow CH_3{-}CH_2{-}CH_2{-}\underset{|}{CH_2}$

(6) $CH_3{-}CH_2{-}CH_2{-}\underset{|}{CH_2} + H_2 \rightarrow CH_3{-}CH_2{-}CH_2{-}CH_3 + H$

II. (1) $CH_2{=}CH_2 + e' \longrightarrow CH_2{=}\underset{|}{CH} + H + e$

(2) $H + CH_2{=}\underset{|}{CH} \longrightarrow CH_2{=}\underset{\|}{C} + H_2 \longrightarrow CH{\equiv}CH + H_2$

(3) $CH{\equiv}CH + H \longrightarrow H_2 + CH{\equiv}\underset{|}{C}$

(4) $CH{\equiv}\underset{|}{C} + CH{\equiv}CH \longrightarrow CH{\equiv}C{-}CH{=}\underset{|}{CH}$

(5) $CH{\equiv}C{-}CH{=}\underset{|}{CH} + H_2 \longrightarrow CH{\equiv}C{-}CH{=}CH_2 + H$

(6) $CH{\equiv}C{-}CH{=}CH_2 + H \longrightarrow CH_2{=}\underset{|}{C}{-}CH{=}CH_2$

(7) $CH_2{=}\underset{|}{C}{-}CH{=}CH_2 + H_2 \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + H$

$$\text{III.}\quad (1)\quad CH_2{=}CH_2 + e' \longrightarrow CH_2{=}\underset{|}{C}H + H + e$$

$$(2)\quad H + CH_2{=}\underset{|}{C}H \longrightarrow CH_2{=}\underset{\|}{C} + H_2 \longrightarrow CH{\equiv}CH + H_2$$

$$(3)\quad CH_2{=}\underset{|}{C}H + CH{\equiv}CH \longrightarrow CH_2{=}CH{-}CH{=}\underset{|}{C}H$$

$$(4)\quad CH_2{=}CH{-}CH{=}\underset{|}{C}H + H_2 \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + H$$

Equation 1 represents the action of an "activated electron" or "activated particle" upon ethene to form a vinyl radical. Type I chain reactions are equivalent to the process,

$$2CH_2{=}CH_2 + H_2 \rightarrow CH_3{-}CH_2{-}CH_2{-}CH_3$$

upon which is superimposed the extra step:

$$CH_2{=}CH_2 \rightarrow CH_2{=}\underset{|}{C}H + \underset{|}{H}$$

Type II chain reactions represent the over-all process,

$$CH_2{=}CH_2 + CH{\equiv}CH \rightarrow CH_2{=}CH{-}CH{=}CH_2$$

whereas those of Type III correspond to:

$$CH_2{=}CH_2 + CH_2{=}\underset{|}{C}H \rightarrow CH_2{=}CH{-}CH{=}CH_2 + \underset{|}{H}$$

All three types of chain reactions are improperly balanced for ethene *per se* processes, although they could be compounded in the following manner:

$$4CH_2{=}CH_2 \rightarrow CH_3{-}CH_2{-}CH_2{-}CH_3 + CH_2{=}CH{-}CH{=}CH_2$$

We presume that thermal conversion is too rapid for any of the three types of chain reactions to become operative and point out that an activated C—H bond explains the results of exposure to high-frequency discharges just as well as chain reactions do (154).

b. Propene

The thermal conversion of propene at 650–1400°C. is an interesting process, though difficult to explain on a mechanistic basis. Wheeler and Wood take the viewpoint that propene primarily decomposes into ethene and butene (158):

$$2C_3H_6 \rightarrow C_2H_4 + C_4H_8$$

Dehydrogenation of butene into butadiene follows. In the presence of hydrogen, some propene may decompose through the scission of the carbon chain at the C—C bond, forming radicals that hydrogenate to methane and ethene:

$$CH_3{-}CH{=}CH_2 \rightarrow \underset{|}{C}H_3 + \underset{|}{C}H{=}CH_2 \xrightarrow{H_2} CH_4 + C_2H_4$$

Ethene from propene decomposition could produce butadiene by polymerization to butene followed by dehydrogenation.

The proposed primary reaction for propene conversion is worthy of discussion. It may be regarded as a bimolecular exchange of a free methyl radical and atomic hydrogen between propene molecules (ionic formulations appear formidable):

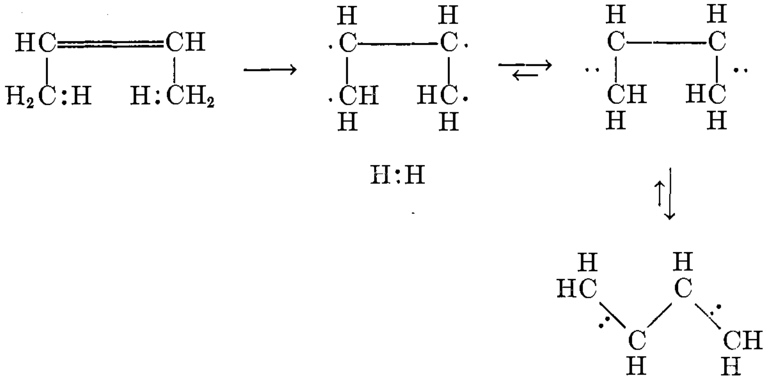
$$\underline{CH_2{=}HC\cdot}|\cdot CH_3 + |\underline{H\cdot}|\cdot CH_2{-}CH{=}CH_2 \longrightarrow$$

$$\underset{\text{Ethene}}{CH_2{=}HC{:}H} + \underset{\text{Butene-1}}{H_3C{:}CH_2{-}CH{=}CH_2}$$

$$\underline{CH_2{=}HC\cdot}|\cdot CH_3 + |\underline{H\cdot}|\cdot CH{=}CH{-}CH_3 \longrightarrow$$

$$\underset{\text{Ethene}}{CH_2{=}HC{:}H} + \underset{\text{Butene-2}}{H_3C{:}CH{=}CH{-}CH_3}$$

Because of reëstablishment of bonds qualitatively and quantitatively, both processes would be thermoneutral in character. According to the equations, butene-1 or butene-2 would be the intermediate for butadiene formation, depending on the type of hydrogen atom scission. Schmidt's double-bond rule suggests that butene-1 is the principal intermediary product, although the required demethylation or dehydrogenation beginning with loss of a 3-position hydrogen atom is enigmatic. This alkene, however, is less rapidly converted (155) into butadiene at 1100°C. than is butene-2, which suggests that the latter isomer may be the precursor. Moreover, this view is fortified by the occurrence of an isomerization of butene-1 into butene-2 under thermal conditions (38). The investigated temperature range (650–1400°C.) for propene conversion (33) is higher than that for butene-1 isomerization (400–700°C.), so that a positive decision in favor of 1,4 dehydrogenation cannot be made at present. If 1,4 loss of hydrogen occurs, *cis*-butadiene is formed from *cis*-butene-2 and immediately leads to the ordinary *cis* and *trans* mixture:



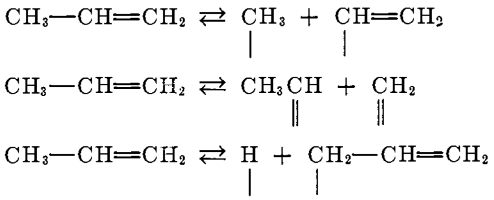
A third bimolecular formulation is that of Frolich, Simard, and White (55) and of Schneider and Frolich (142):

$$\underline{CH_2{=}HC\cdot}|\cdot CH_3 + H_3C\cdot|\underline{\cdot CH{=}CH_2} \rightarrow \underset{\text{Ethane}}{H_3C{:}CH_3} + \underset{\text{Butadiene}}{CH_2{=}HC{:}CH{=}CH_2}$$

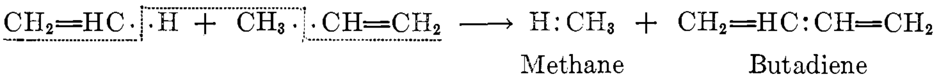
This process departs twice from the β-bond rule of Schmidt. Schneider and Frolich extrapolated their data back to zero per cent cracking and drew the following conclusions:

> "For each 100 moles of propylene reacting, 23 or 24 moles of both butylene and ethylene are formed as initial products. Hence, it must be concluded that about 48 per cent of the propylene reacts according to the equation
>
> $$2C_3H_6 \rightarrow C_2H_4 + C_4H_8.$$
>
> Likewise, it seems that about 10 per cent goes to form ethane and butadiene by the reaction
>
> $$2C_3H_6 \rightarrow C_2H_6 + C_4H_6."$$

These "initial" reactions were criticized as follows (29):

> "If the above equation represents the initial steps in the decomposition, one would expect the reactions to be bimolecular. However, it was observed that 'the amount of propylene reacting is actually increased threefold' when its partial pressure was reduced from one to one-eighth atmosphere by dilution with an inert gas. This indicates that the hydrocarbons which appear on the graph as initial products were not formed as the immediate result of bimolecular collisions between propylene molecules, but rather in a series of changes in which 'free radicals or activated molecules' are the intermediates. If the initial steps in the decomposition are represented by the equations:
>
> 
>
> $$CH_3{-}CH{=}CH_2 \rightleftarrows \underset{|}{CH_3} + \underset{|}{CH}{=}CH_2$$
>
> $$CH_3{-}CH{=}CH_2 \rightleftarrows \underset{\|}{CH_3CH} + \underset{\|}{CH_2}$$
>
> $$CH_3{-}CH{=}CH_2 \rightleftarrows \underset{|}{H} + \underset{|}{CH_2}{-}CH{=}CH_2$$
>
> there should be no decrease in the reaction rate when the partial pressure of propylene is lowered from one to one-eighth atmosphere, whereas a retardation rather than the observed increase in the reaction rate would be expected if the initial steps in the decomposition are bimolecular reactions between propylene molecules."

A fourth bimolecular formulation takes advantage of the simultaneous presence of ethene and propene from preliminary reactions (55):



$$\underline{CH_2{=}HC\cdot}\boxed{\cdot H + CH_3\cdot}\underline{\cdot CH{=}CH_2} \longrightarrow \underset{\text{Methane}}{H{:}CH_3} + \underset{\text{Butadiene}}{CH_2{=}HC{:}CH{=}CH_2}$$

An entirely different view of propene conversion was taken in Tropsch's study (155):

> "Data show that under mild conditions there is a contraction; and as the conditions become more severe, a point is reached where there is no change in volume, showing that the expansion which results from decomposition is equal to the contraction in volume from polymerization (112). If, however, the conditions are still more severe, decomposition will mask the polymerization and only the increase in volume will be observed. . . .
>
> "The polymer obtained in the primary reaction would be unstable under the experimental conditions, partly decomposing to yield the observed gaseous products."

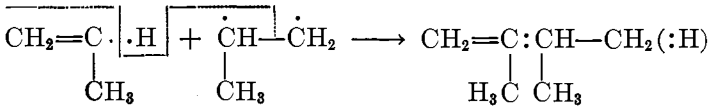
One may assume, therefore, that propene undergoes a dimerization into hexene-1, hexene-2, and 2,3-dimethylbutene-1,

$$\overline{\mathrm{CH_2{=}CH{-}H_2C\cdot}}\,\boxed{\mathrm{\cdot H}}\;+\;\overline{\dot{\mathrm{C}}\mathrm{H_2}}{\mid}\dot{\mathrm{C}}\mathrm{H{-}CH_3}\longrightarrow \mathrm{CH_2{=}CH{-}H_2C{:}CH_2{-}HC({:}H){-}CH_3}$$

Hexene-1

$$\overline{\mathrm{CH_3{-}CH{=}HC\cdot}}\,\boxed{\mathrm{\cdot H}}\;+\;\overline{\dot{\mathrm{C}}\mathrm{H_2}}{\mid}\dot{\mathrm{C}}\mathrm{H{-}CH_3}\longrightarrow \mathrm{CH_3{-}CH{=}HC{:}CH_2{-}HC({:}H){-}CH_3}$$

Hexene-2



$$\overline{\underset{\mathrm{CH_3}}{\mathrm{CH_2{=}C\cdot}}}\,\boxed{\mathrm{\cdot H}}\;+\;\overline{\underset{\mathrm{CH_3}}{\dot{\mathrm{C}}\mathrm{H}}}{\mid}\dot{\mathrm{C}}\mathrm{H_2}\longrightarrow \mathrm{CH_2{=}}\underset{\mathrm{H_3C}}{\mathrm{C}}{:}\underset{\mathrm{CH_3}}{\mathrm{CH}}\mathrm{{-}CH_2({:}H)}$$

2,3-Dimethylbutene-1

and that this reaction is competitive with formation of free vinyl plus free methyl radicals:

$$\mathrm{CH_2{=}CH\cdot\cdot CH_3 \rightarrow CH_2{=}}\dot{\mathrm{C}}\mathrm{H} + \dot{\mathrm{C}}\mathrm{H_3}$$

The transfer of a hydrogen atom can be made the last step:

$$\mathrm{CH_3{-}}\dot{\mathrm{C}}\mathrm{H{-}H_2}\dot{\mathrm{C}} + \dot{\mathrm{C}}\mathrm{H_2{-}}\dot{\mathrm{C}}\mathrm{H{-}CH_3}\longrightarrow \mathrm{CH_3{-}}\dot{\mathrm{C}}\mathrm{H{-}H_2C{:}CH_2{-}}\dot{\mathrm{C}}\mathrm{H{-}CH_3}$$

Hexane-2,5-diyl

$$\mathrm{CH_3{-}}\dot{\mathrm{C}}\mathrm{H{-}H_2C{:}CH_2{-}}\dot{\mathrm{C}}\mathrm{H{-}CH_3}\longrightarrow \mathrm{CH_3{-}CH{=}HC{-}CH_2{-}CH_2{-}CH_3}$$

Each of these six equations can be considered as representing the beginning of a process yielding butadiene. The succeeding steps will be considered next.

At 650–700°C. hexene-1 forms a small amount (106) of butadiene such as would be expected of a substance related to propene. According to Schmidt's double-bond rule, activation of hexene-1, followed by scission, should give a mixture of prop-1-en-3-yl ($CH_2{=}CH\dot{C}H_2$) and *n*-propyl or, less favorably, one of hex-1-en-3-yl ($CH_2{=}CH\dot{C}HCH_2CH_2CH_3$) plus a hydrogen atom. Butadiene is not expected. We postulate, therefore, an isomerization of hexene-1 into hexene-2 under thermal conditions in the conversion of propene. The corresponding catalytic isomerization is well established but is competitive with the formation of still other isomers (39).

Hexene-2 has not been tested for ability to form butadiene. Theoretically, it is expected to undergo initial scissions as follows:

$$CH_3-CH=CH-CH_2\cdot\cdot CH_2-CH_3 \longrightarrow$$

$$CH_3-CH=CH-\dot{C}H_2 + \dot{C}H_2-CH_3$$

$$H\cdot\cdot CH_2-CH=CH-CH_2-CH_2-CH_3 \longrightarrow$$

$$\dot{H} + \dot{C}H_2-CH=CH-CH_2-CH_2-CH_3$$

$$H\cdot\cdot CH_2-CH\overset{:}{-}CH-CH_2\cdot\cdot CH_2-CH_3 \longrightarrow$$

$$\dot{H} + \underset{\displaystyle CH_2=CH-CH=CH_2}{\underset{\upharpoonleft\downharpoonright}{\dot{C}H_2-\dot{C}H-\dot{C}H-\dot{C}H_2}} + \dot{C}H_2-CH_3$$

These equations are arranged in order of increasing energy requirement, i.e., scission of one C—C bond, of one C—H bond, or of one C—C bond plus one C—H bond plus the "unsaturated half" of a C=C linkage. Further conversion of the free radical products would yield butadiene in the manner:

$$H\cdot\cdot CH_2-CH=CH-\dot{C}H_2 \rightarrow \dot{H} + \dot{C}H_2-CH=CH-\dot{C}H_2$$

$$\dot{C}H_2-CH=CH-CH_2\cdot\cdot CH_2-CH_3 \rightarrow \dot{C}H_2-CH=CH-\dot{C}H_2 + \dot{C}H_2-CH_3$$

These equations are given in order of decreasing endothermicity. Ethyl radicals would unite with or lose hydrogen atoms, but could also form *n*-butane:

$$\dot{C}H_2-CH_3 + \dot{H} \rightarrow H{:}CH_2-CH_3 \text{ (ethane)}$$

$$\dot{C}H_2-CH_3 \rightarrow \dot{H} + CH_2\overset{:}{-}CH_2 \text{ (ethene)}$$

$$2\dot{C}H_2-CH_3 \rightarrow CH_3-CH_2{:}CH_2-CH_3 \text{ (butane)}$$

$$2\dot{H} \rightarrow H{:}H$$

Therefore, the conversions of hexene-2 are expected to follow the following courses:

$$CH_3-CH=CH-CH_2-CH_2-CH_3 \rightarrow CH_2=CH-CH=CH_2 + C_2H_6$$

$$2CH_3-CH=CH-CH_2-CH_2-CH_3 \rightarrow 2CH_2=CH-CH=CH_2 + CH_3-CH_2-CH_2-CH_3 + H_2$$

$$CH_3-CH=CH-CH_2-CH_2-CH_3 \rightarrow CH_2=CH-CH=CH_2 + C_2H_4 + H_2$$

The arrangement is in order of increasing endothermicity, i.e., decreasing probability of occurrence unless the thermal input is excessive.

Over-all equations are now available for the conversions of propene passing through a hexene-1 or hexene-2 stage:

$$\mathrm{2CH_2{=}CH{-}CH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + C_2H_6}$$

$$\mathrm{4CH_2{=}CH{-}CH_3 \rightarrow 2CH_2{=}CH{-}CH{=}CH_2 + C_4H_{10} + H_2}$$

$$\mathrm{2CH_2{=}CH{-}CH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + C_2H_4 + H_2}$$

Hexene-3, attributable to isomerization of hexene-1 or hexene-2, should yield butadiene by demethylation:

$$\mathrm{H_3C\cdot\cdot CH_2{-}CH\overset{:}{-}CH{-}H_2C\cdot\cdot CH_3 \rightarrow 2\dot{C}H_3 + \dot{C}H_2{-}\dot{C}H{-}\dot{C}H{-}\dot{C}H_2}$$

$$\mathrm{\rightleftarrows\; CH_2{=}CH{-}CH{=}CH_2}$$

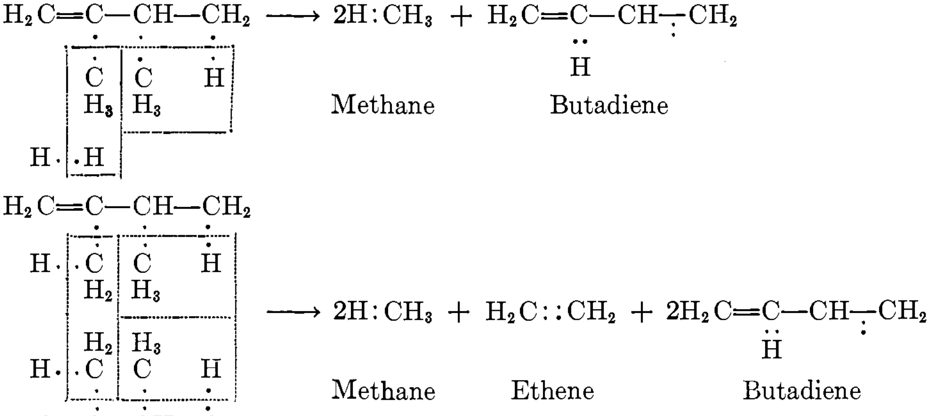
$$\mathrm{2\dot{C}H_3 \rightarrow H_3C{:}CH_3\ (ethane)}$$

The over-all equation is:

$$\mathrm{2CH_2{=}CH{-}CH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + C_2H_6}$$

Hexene-3 conversion is expected to be slightly exothermic. Confirmatory experimental work is unavailable.

2,3-Dimethylbutene-1 and 2,3-dimethylbutene-2 have not been considered in the literature from the conversion viewpoint. The first alkene would require demethylation, probably once by elimination of methane and once by hydrogenolysis or by formation of ethene:

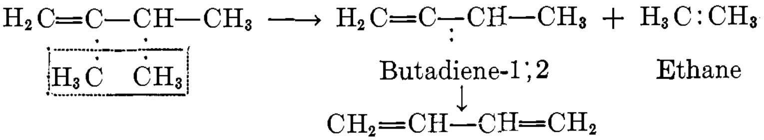


$$\mathrm{H_2C{=}C{-}CH{-}CH_2 \longrightarrow 2H{:}CH_3 + H_2C{=}\underset{H}{\ddot{C}}{-}CH\dot{-}CH_2}$$

$$\mathrm{\longrightarrow 2H{:}CH_3 + H_2C{:}{:}CH_2 + 2H_2C{=}\underset{H}{\ddot{C}}{-}CH\dot{-}CH_2}$$

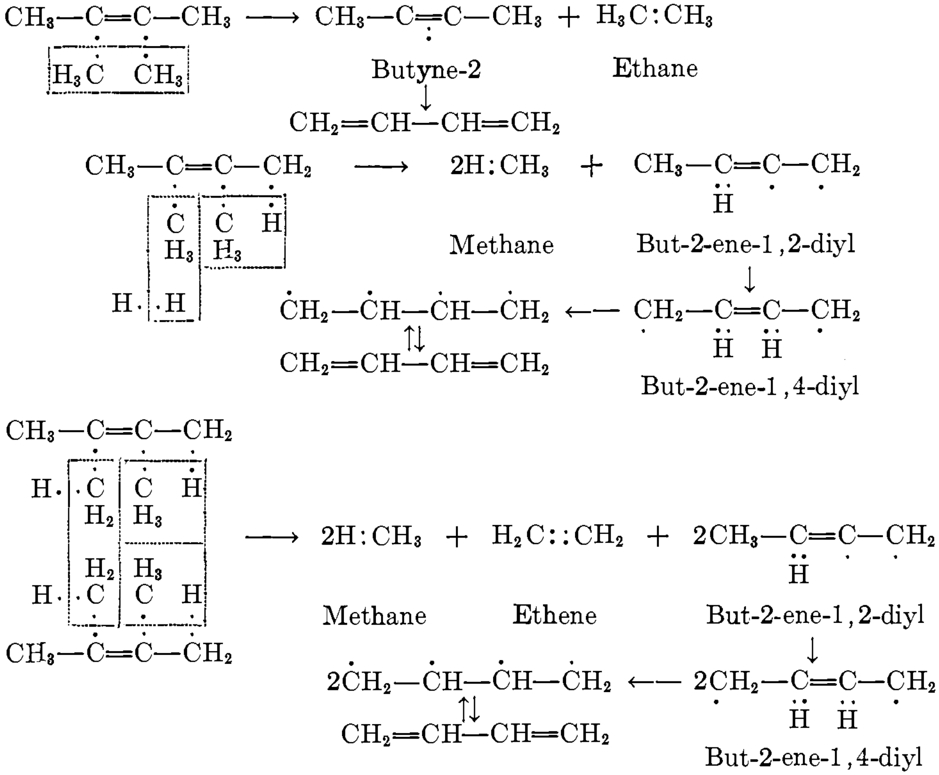
An objection may be raised against the hydrogenolysis of a methyl group without saturation of a double bond in juxtaposition. Both hydrogen reactions would be exothermic, the latter predominantly so. Therefore, ethene formation through the union of methylene groups as high-temperature scission products is also postulated. Removal of the 3-methyl group would be in conformity with

Schmidt's double-bond rule. That of the 2-methyl group would be contrariwise, although probable at high temperatures. A concomitant removal of both methyl groups, forming butadiene-1,2 and ethane, would still require a final isomerization:



The proximity of methyl groups in the 2- and 3-positions would favor the conversion, and prior dissociation of the 3-methyl radical in conformity with the β-bond rule might make it possible.

2,3-Dimethylbutene-2 should be convertible into butadiene after isomerization to the alkene-1 or by any of the following processes:



A hydrogen atmosphere is indicated for the second process, rather than dependence upon the operation of local dehydrogenations.

We now return to the scission of propene into free vinyl and free methyl radicals, a change which was assumed to be competitive with the polymerization of propene into hexenes. Vinyl radicals would yield butadiene through electronic coupling:

$$CH_2{=}H\dot{C} + \dot{C}H{=}CH_2 \rightarrow CH_2{=}HC{:}CH{=}CH_2$$

An inspection of the over-all equation,

$$2CH_2{=}CH{-}CH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + CH_3{-}CH_3$$

indicates that equal numbers of C—C bonds are broken and re-formed. Successful conversion of propene requires a preferential activation and scission of the methyl-to-vinyl linkage. The new bond formation that follows should be facilitated by instantaneous removal of the excitation energy and through the introduction of endothermic processes immediately after the scission. In support of the free-radical formulation there can be cited the results of cracking propene at 600°C. in the presence of hydrogen (75). These showed greatly increased percentages of methane and ethene over yields from propene alone.

c. Butenes

Butene-1 apparently requires only dehydrogenation to form butadiene:

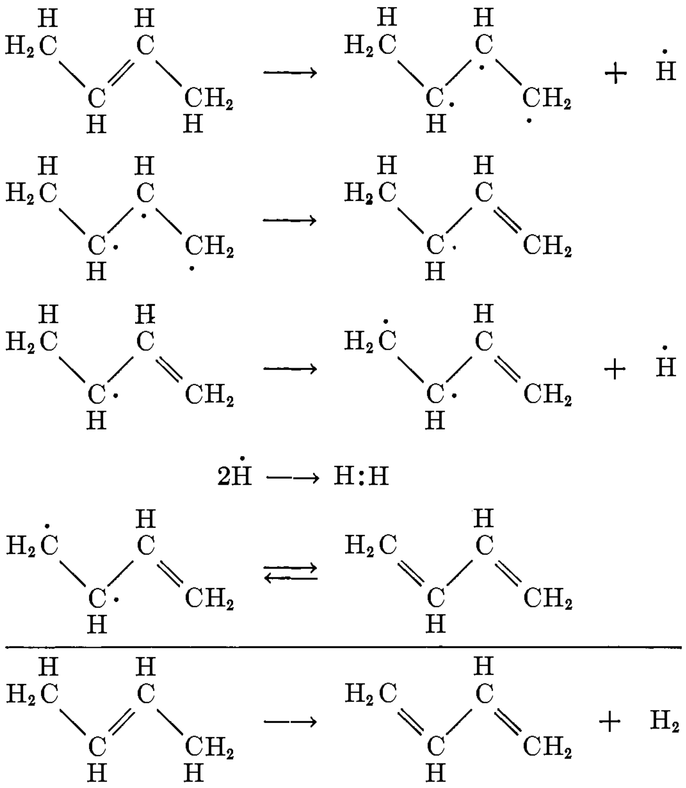
$$\begin{array}{lcl} CH_2{=}CH{-}CH_2{-}CH_3 & \longrightarrow & CH_2{=}CH{-}\dot{C}H{-}CH_3 + \dot{H} \\ CH_2{=}CH{-}\dot{C}H{-}CH_3 & \longrightarrow & CH_2{=}CH{-}\dot{C}H{-}\dot{C}H_2 + \dot{H} \\ & 2\dot{H} \longrightarrow & H{:}H \\ CH_2{=}CH{-}\dot{C}H{-}\dot{C}H_2 & \rightleftarrows & CH_2{=}CH{-}CH{=}CH_2 \\ \hline CH_2{=}CH{-}CH_2{-}CH_3 & \longrightarrow & CH_2{=}CH{-}CH{=}CH_2 + H_2 \end{array}$$

A conversion through loss of atomic hydrogens is illustrated; the "stabilization" of but-1-ene-3,4-diyl ($CH_2{=}CH\dot{C}H\dot{C}H_2$) into the covalent alkadiene cannot be regarded as an additional step. Schmidt's double-bond rule suggests that but-1-en-3-yl ($CH_2{=}CH\dot{C}HCH_3$) rather than but-1-en-4-yl ($CH_2{=}CHCH_2\dot{C}H_2$) is the intermediate yielding the butenediyl. The entire dehydrogenation can be conducted thermally (33) or catalytically (6, 36).

Butene-2 requires 1,4 dehydrogenation and central bond activation for conversion into butadiene:

$$\begin{array}{lcl} CH_3{-}CH{=}CH{-}CH_3 & \longrightarrow & \dot{C}H_2{-}\dot{C}H{-}\dot{C}H{-}\dot{C}H_2 + H{:}H \\ \dot{C}H_2{-}\dot{C}H{-}\dot{C}H{-}\dot{C}H_2 & \rightleftarrows & CH_2{=}CH{-}CH{=}CH_2 \\ \hline CH_3{-}CH{=}CH{-}CH_3 & \longrightarrow & CH_2{=}CH{-}CH{=}CH_2 + H_2 \end{array}$$

In the discussion on propene conversion, a formulation for 1,4 dehydrogenation of *cis*-butene-2 to give *cis*-butadiene and eventually the *trans*-alkadiene was presented. A direct conversion of *trans*-butene-2 into *trans*-butadiene appears less probable:



The conversion of butene-2 may be conducted thermally (33) or catalytically (36). A catalyst facilitates the steps indicated for thermal conversion by aiding or performing the following operations: (*a*) activation of the double bond, (*b*) removal of atomic hydrogen from butene-2 or but-1-en-3-yl ($CH_2{=}CH\dot{C}HCH_3$), (*c*) formation of but-1-en-3-yl from butane-1,2,3-triyl ($\dot{C}H_2\dot{C}H\dot{C}HCH_3$), (*d*) transfer of the energy released upon but-1-en-3-yl formation to the C—H bond in the 4-position, and (*e*) union of atomic hydrogens to form molecules.

In practice, it is not necessary to utilize an individual butene. Much data are available concerning the catalytic dehydrogenation of mixtures of butene-1 and butene-2 over chromia or other catalysts (36, 57, 109). Limited data are concerned with the corresponding thermal treatment (33). Even 2-methylpropene has been converted into butadiene and other products (155). A study of the equilibrium dehydrogenation of butene-1 and butene-2 into butadiene at 480–534°C. over a chromia catalyst indicates that the reaction is about 29 kcal. endothermic (19).

d. Pentenes

Pentene-1 and pentene-2 are almost equally convertible into butadiene at 600°C. or 650°C. in the presence of steam (106). A similar conversion of pentene-2 occurred at 600°C. in the absence of steam (112). The mechanism of the last reaction was formulated as follows:

$$\mathrm{CH_3CH{=}CH\underset{|}{C}H_2CH_3 \rightarrow CH_3CH{=}CH\underset{|}{C}H_2 + \underset{|}{C}H_3}$$

$$\mathrm{CH_3CH{=}CH\underset{|}{C}H_2 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H}$$

Formation of methane and butene-2 was ascribed to hydrogenation of primary radicals by hydrogen released in but-2-en-1-yl conversion or carbon deposition:

$$\mathrm{CH_3CH{=}CH\underset{|}{C}H_2 + \underset{|}{C}H_3 + 2H \rightarrow CH_3CH{=}CHCH_3 + CH_4}$$

The conversion of pentene-1 into butadiene may proceed in two ways: A preliminary isomerization into pentene-2 suggests itself from the work of Hurd (70, 74). An alternative mechanism, available for high thermal input rates, consists of demethanation by (*a*) activation of the double bond, (*b*) loss of a hydrogen atom in the β-position to the activated double bond, (*c*) formation of pent-2-en-1-yl ($\mathrm{\dot{C}H_2CH{=}CHCH_2CH_3}$) from pentane-1,2,3-triyl ($\mathrm{\dot{C}H_2\dot{C}H\dot{C}HCH_2CH_3}$), (*d*) full activation of the C—C bond holding the terminal methyl group, and (*e*) union of atomic hydrogen and the free methyl radical to form methane:

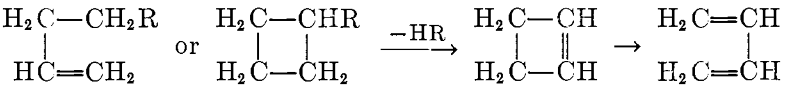
$$\begin{gathered}
\mathrm{\dot{C}H_2{-}\dot{C}H{-}\overset{H}{\overset{\vdots}{C}}H{-}CH_2{-}CH_3 \rightarrow \dot{C}H_2{-}\dot{C}H{-}\dot{C}H{-}CH_2{-}CH_3 + \dot{H}} \\
\mathrm{\dot{C}H_2{-}\dot{C}H{-}\dot{C}H{-}CH_2{-}CH_3 \rightarrow \dot{C}H_2{-}CH{=}CH{-}CH_2{-}CH_3} \\
\mathrm{\dot{C}H_2{-}CH{=}CH{-}CH_2\cdot\cdot CH_3 \rightarrow \dot{C}H_2{-}CH{=}CH{-}\dot{C}H_2 + \dot{C}H_3} \\
\mathrm{\dot{C}H_2{-}CH{=}CH{-}\dot{C}H_2 \rightleftarrows \dot{C}H_2{-}\dot{C}H{-}\dot{C}H{-}\dot{C}H_2 \rightleftarrows CH_2{=}CH{-}CH{=}CH_2} \\
\mathrm{\dot{H} + \dot{C}H_3 \rightarrow H{:}CH_3}
\end{gathered}$$

Demethylation of pentane-1,2,3-triyl should be possible also, but this would probably require a higher temperature than 600°C.

To explain the frequent and then (1913) often unexpected formation of butadiene in the thermal treatment of straight-chain or cyclic hydrocarbons, Ostromyslenskiĭ formulated the following rule (122):

> "Straight chain hydrocarbons containing one double bond or saturated cyclic hydrocarbons, regardless of their structure or molecular weight, eliminate under the action of high temperature a saturated hydrocarbon and not hydrogen. In this reaction, side-chain radicals are split off, including all carbon atoms with the exception of four, which include the two carbon atoms connected by the double bond, thus forming butadiene."

Details of the foregoing conversions were purposely omitted in order to avoid complicating the discussion. The rôles of isomerization and of cyclobutene formation, however, were considered:



According to Ostromyslenskiĭ, alkenes and cyclanes containing five or more carbon atoms per molecule must persistently retain four such atoms in thermal decomposition. In some cases, isomerization of the primary product was postulated, such that a linear chain of four carbon atoms results. Also, in hydrocarbons above butene and cyclobutane in size, demethanation and de-ethanation must occur more easily than elimination of molecular hydrogen. The rule does not mention hydrocarbons with less than four carbon atoms per molecule; it was presumed that these members easily condense at high temperatures into convertible hydrocarbons. As examples of the decomposition of alkenes into butadiene, the conversions of 3-methylbutene-1 and 2-methylbutene-2 were cited (122):

$$CH_2{=}CH{-}CH(CH_3)_2 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + CH_4$$

$$(CH_3)_2C{=}CH{-}CH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + CH_4$$

A later publication (124) omits the foregoing rule and replaces it by the statement, "elimination of RH (R being an alkyl group) from straight chain hydrocarbons containing a single double bond," a process that was expressed by the equation:

$$RC_4H_7 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + RH$$

where C_4H_7 is presumably any linear butenyl group (i.e., but-1-en-1-, 2-, 3-, or 4-yl and but-2-en-1- or 2-yl), and that was substantiated by a reaction of new type, namely, a depolymerization of alkenes accompanied by dehydrogenation or dealkanation:

$$C_8H_{16}\ (\text{"dibutene"}) \rightarrow 2CH_2{=}CH{-}CH{=}CH_2 + 2H_2$$

$$C_{10}H_{20}\ (\text{"diamylene"}) \rightarrow 2CH_2{=}CH{-}CH{=}CH_2 + 2CH_4$$

The structures of the two alkenes were not considered. Formation of 2-methylbutadiene-1,3 (i.e., isoprene) in the pyrolysis of its natural aliphatic dimer, myrcene, was admitted but not regarded as atypical.. However, the views of Perkin and Weizmann (130), Staudinger (47), and others (119) regarding enhanced dehydrogenation of branched pentenes into 2-methylbutadiene-1,3 were claimed to be erroneous. Schotz disagrees with this claim (143):

> "Suppose Ostromyslenskiĭ's experiments are correct, the apparent contradiction can be explained quite simply: We have seen in discussing the preparation of isoprene from petro-

leum according to French Patent Specification 435,312 that it is an established fact that trimethylethylene is produced from two other amylenes under certain conditions, and no doubt may also be transformed into isomeric compounds. Owing to the unstable nature of these unsaturated bodies the results depend on so many factors that it is unwise to doubt observations made by chemists of high standing."

Ostromyslenskiĭ's rule (122) can be regarded as a foreshadowing of our C_4 directive fragmentation theory, which is more applicable to linear than to cyclic molecules. Ring strain, despite its neglect by Ostromyslenskiĭ, is an important factor governing the conversion of cyclic hydrocarbons.

e. Hexadecene

Hexadecene is the largest alkene yet investigated from the standpoint of butadiene formation. One group of investigators obtained a 1 per cent yield at 550°C. and interpreted its data by a series of equations (56):

$$(1)\quad CH_3 \mid CH_2-(CH_2)_{12}-CH=CH_2 \rightarrow$$
$$CH_2=CH-(CH_2)_{11}-CH=CH_2 + CH_4$$

$$(2)\quad CH_3-CH_2 \mid CH_2-CH_2-(CH_2)_{10}-CH=CH_2 \rightarrow$$
$$CH_2=CH-(CH_2)_{10}-CH=CH_2 + CH_3-CH_3$$

$$(3)\quad CH_3-CH_2-CH_2 \mid CH_2-CH_2-(CH_2)_9-CH=CH_2 \rightarrow$$
$$CH_2=CH-(CH_2)_9-CH=CH_2 + CH_3-CH_2-CH_3, \text{ etc.}$$

$$(4)\quad CH_2=CH-(CH_2)_{10}-CH_2 \mid CH=CH_2 \rightarrow$$
$$CH_2=CH-(CH_2)_9-CH=CH_2 + CH_2=CH_2$$

$$(5)\quad CH_2=CH-(CH_2)_9-CH_2 \mid CH_2-CH=CH_2 \rightarrow$$
$$CH_2=CH-(CH_2)_8-CH=CH_2 + CH_3-CH=CH_2$$

$$(6)\quad CH_2=CH-(CH_2)_8-CH_2 \mid CH_2-CH_2-CH=CH_2 \rightarrow$$
$$CH_2=CH-(CH_2)_7-CH=CH_2 + CH_3-CH_2-CH=CH_2, \text{ etc.}$$

$$(7)\quad CH_2=CH-CH_2-CH_2 \mid CH=CH_2 \rightarrow$$
$$CH_2=CH-CH=CH_2 + CH_2=CH_2, \text{ etc.}$$

$$(8)\quad CH_2=CH-(CH_2)_8-CH_2 \mid CH_2-CH_2-CH=CH_2 \rightarrow$$
$$CH_2=CH-(CH_2)_7-CH=CH_2 + CH_2=CH-CH=CH_2$$

Equations 1, 2, and 3 represent supposed changes in the primary reaction as the temperature or thermal input increases. The resulting alkadienes were assumed to undergo secondary reactions according to equations 4, 5, and 6. Tertiary reactions, 7 and 8, were proposed as the final phases of thermal degradation.

The foregoing equations admit of three distinct ways of butadiene formation:

$$\begin{aligned}
&(9).\ CH_3{-}(CH_2)_{13}{-}CH{=}CH_2 \rightarrow CH_2{=}CH{-}(CH_2)_2{-}CH{=}CH_2\\
&\qquad\qquad\qquad\qquad\qquad\qquad + CH_3{-}(CH_2)_8{-}CH_3\\
&(7)\ CH_2{=}CH{-}(CH_2)_2{-}CH{=}CH_2 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH_2
\end{aligned}$$

$$\begin{aligned}
&(1)\ CH_3{-}CH_2{-}(CH_2)_{12}{-}CH{=}CH_2 \rightarrow CH_2{=}CH{-}(CH_2)_{11}{-}CH{=}CH_2\\
&\qquad\qquad\qquad\qquad\qquad\qquad + CH_4\\
&(10)\ CH_2{=}CH{-}(CH_2)_{11}{-}CH{=}CH_2 \rightarrow CH_2{=}CH{-}(CH_2)_2{-}CH{=}CH_2\\
&\qquad\qquad\qquad\qquad\qquad\qquad + CH_3{-}(CH_2)_6{-}CH{=}CH_2\\
&(7)\ CH_2{=}CH{-}(CH_2)_2{-}CH{=}CH_2 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH_2
\end{aligned}$$

$$\begin{aligned}
&(1)\ CH_3{-}CH_2{-}(CH_2)_{12}{-}CH{=}CH_2 \rightarrow CH_2{=}CH{-}(CH_2)_{11}{-}CH{=}CH_2\\
&\qquad\qquad\qquad\qquad\qquad\qquad + CH_4\\
&(11)\ CH_2{=}CH{-}(CH_2)_{11}{-}CH{=}CH_2 \rightarrow CH_2{=}CH{-}(CH_2)_8{-}CH_3\\
&\qquad\qquad\qquad\qquad\qquad\qquad + CH_2{=}CH{-}CH{=}CH_2
\end{aligned}$$

Equation 11 replaces equation 8, which has a hydrogen deficiency as originally written. Otherwise, hydrogen gas would have to be included as a product and its formation specifically provided for in the investigators' interpretation.

We now proceed to discuss the three implied mechanisms. In all cases, the first reaction is given as a dealkanation. The final reaction is represented as the debutadienation of a higher alkadiene.

Demethanation of hexadecene-1 (equation 1) is probably an unimportant "primary" reaction. Its complexity, moreover, is indicated by the required operation on linkages, namely, breakage of a C—C bond, then of a C—H bond, followed by closure of atomic hydrogen upon the free methyl radical to form methane and by formation of a double bond. In the cracking of hexadecene under pressure, the carbon chain seems to break near the double bond (67). If the hexadecene molecule introduced originally has and thereafter retains its double bond in the terminal position, demethanation has the advantage of forming two symmetrical products. On the other hand, demethanation is contrary to several principles already considered. Thus, C_2 directive fragmentation would lead to formation of ethene and its polymers. A C_4 directive fragmentation would easily account for the butadiene production. Its operation would furnish a supply of atomic hydrogen that could cause extensive hydrogenolysis into methane and higher alkanes. Demethanation "at low temperatures" is contrary to Schmidt's double-bond rule, whereby the following products should develop from the several straight-chain hexadecenes that constitute or probably arise from "hexadecene:"

INITIAL HEXADECENE	"PRIMARY" PRODUCTS	
	Unstable	Stabilized
Hexadecene-1..	Prop-1-en-3-yl Tridecyl-1	Propene or propadiene Tridecane or tridecene-1
Hexadecene-2..	Atomic hydrogen But-2-ene-1,4-diyl Dodecyl-1	Hydrogen Butadiene Dodecane or dodecene-1
Hexadecene-3..	Methyl But-2-ene-1,4-diyl Hendecyl-1	Methane or ethane or ethene Butadiene Hendecane or dodecane or hendecene-1
Hexadecene-4..	Ethyl But-2-ene-1,4-diyl Decyl-1	Ethane or butane or ethene Butadiene Decane or dodecane or decene-1
Hexadecene-5..	*n*-Propyl But-2-ene-1,4-diyl Nonyl-1	Propane or hexane or propene Butadiene Nonane or dodecane or nonene-1
Hexadecene-6..	*n*-Butyl But-2-ene-1,4-diyl Octyl-1	Butane or octane or butene-1 Butadiene Octane or dodecane or octene-1
Hexadecene-7..	Pentyl-1 But-2-ene-1,4-diyl Heptyl-1	Pentane or decane or pentene-1 Butadiene Heptane or dodecane or heptene-1
Hexadecene-8..	Hexyl-1 But-2-ene-1,4-diyl	Hexane or dodecane or hexene-1 Butadiene

According to the double-bond rule, the reported pyrolysis products should have had 24.1 weight per cent of butadiene except from unisomerized hexadecene-1. One may assume, therefore, that the formation (observed) of cyclic hydrocarbons was responsible for low yields of this alkadiene at 500–600°C.

Dedecanation of hexadecene-1 to yield hexadiene-1,5 as per equation 9 can be considered as the start of an interesting speculation. The subsequent equation 7 represents the operation of both C_2H_4 and C_4H_6 directive fragmentations. Actually, cyclization products mainly replaced butadiene. Catalytic conversion of hexadecene over neutral or alkaline catalysts devoid of cyclization tendency (40) suggests itself. Inhibitors may be useful.

Denonenation of pentadecadiene-1,14 in the manner of equation 10 was not considered to be an important source of a lower alkadiene. Equation 7, however, was set up as an example of a reaction terminating a degradation series. Equations 1, 10, and 7 obviously represent a minor source of the total butadiene actually produced or producible. More probable ways of formation of this alkadiene are conceivable.

The debutadienation of pentadecadiene-1,14 was neglected by its proposers.

It is best represented according to equation 11 and is an example of C_4H_6 directive fragmentation at the end of a long molecule. Because it does not follow the double-bond rule, we assume that it is operative mainly at high temperatures.

Regarding the possibility of a 48.2, 72.3, or 96.4 weight per cent yield of butadiene from straight-chain hexadecenes, by the formation of two, three, or four molecules of alkadiene per one of alkene, it can be stated that two paths of investigation are available to the researcher. One consists of depolymerization of straight-chain hexadecenes into straight-chain octenes, or even into butenes-1 and -2, prior to dehydrogenation. The other path aims at direct scission of hexadecene into C_4 fragments by selective activation of the molecule. That the latter is not unattainable can be seen from the few methods of increasing molecular energy investigated to date and from the many methods available for delineation of modes of molecular distortion or vibrations.

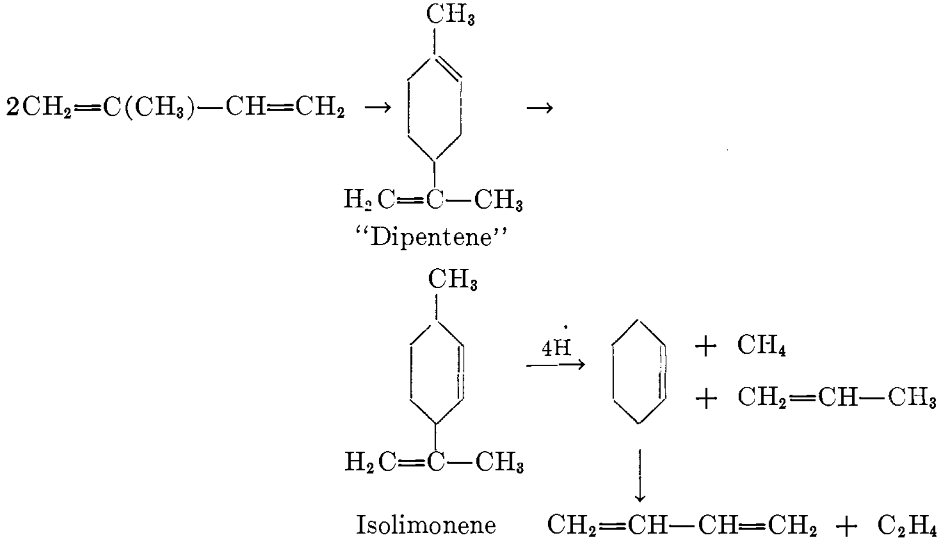
3. Alkadienes

2-Methylbutadiene-1,3 undergoes a slight "demethylenation" to butadiene when passed at 600–820°C. through tubes packed with coke (148). The conversion was believed to be dependent upon a cracking of by-products, including 2-methylbutene-2, hydroaromatic hydrocarbons, and aromatics. For example, 1,4 hydrogenation would give 2-methylbutene-2, which upon demethanation would form butadiene:

$$CH_2{=}C(CH_3){-}CH{=}CH_2 + 2\dot{H} \rightarrow CH_3{-}C(CH_3){=}CH{-}CH_3$$

$$CH_3{-}C(CH_3){=}CH{-}CH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + CH_4$$

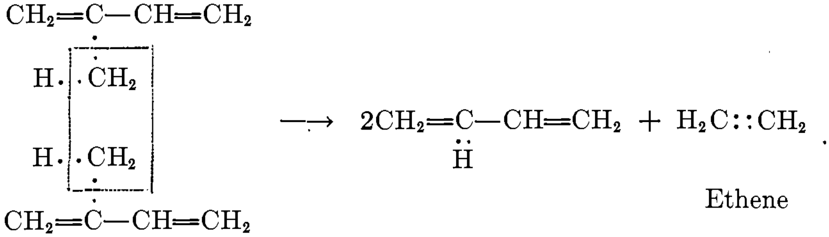
Polymerization of 2-methylbutadiene-1,3 would give limonene-like dimers, and subsequent side-chain scissions could lead to cyclohexene formation, explaining any conversion of "hydroaromatic hydrocarbons:"



"Dipentene"

Isolimonene

An isomerization of dipentene is depicted, so that Schmidt's double-bond rule is satisfied; carbonization would release the four hydrogen atoms required for hydrogenolysis to methane and propene. Cyclohexene due to the hydrogenation of benzene also might be available; it was demonstrated that the cracking of 2-methylbutene-2 gives a tar containing benzene, naphthalene, and anthracene. Cyclohexene is readily converted into a mixture of butadiene and ethene. The present authors favor a direct demethylenation of 2-methylbutadiene-1,3, as follows:

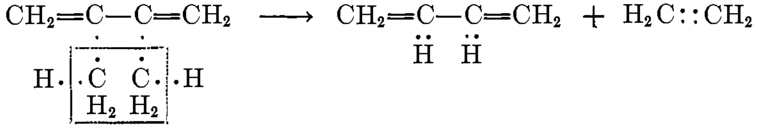


$$2\,CH_2{=}\dot{C}{-}CH{=}CH_2 \;(H\cdot\,\cdot CH_2) \longrightarrow 2CH_2{=}\underset{H}{\ddot{C}}{-}CH{=}CH_2 + H_2C{::}CH_2$$

Ethene

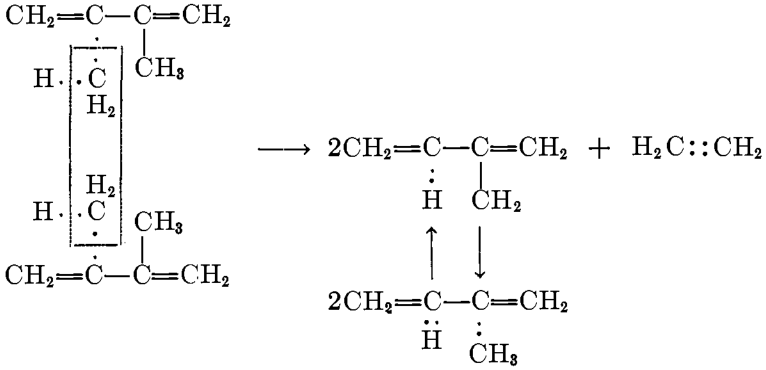
2,3-Dimethylbutadiene-1,3 forms a small amount of butadiene at 700–800°C. (148). In lieu of a conversion proceeding via the tars formed, the following demethylenations can be considered:

(A)



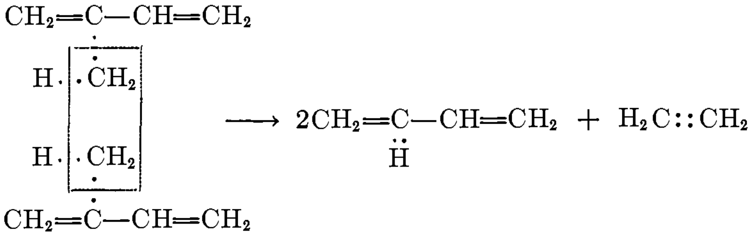
$$CH_2{=}\dot{C}{-}\dot{C}{=}CH_2 \;(H\cdot\,\cdot\underset{H_2}{C}\;\underset{H_2}{C}\cdot\,\cdot H) \longrightarrow CH_2{=}\underset{H}{\ddot{C}}{-}\underset{H}{\ddot{C}}{=}CH_2 + H_2C{::}CH_2$$

(B)



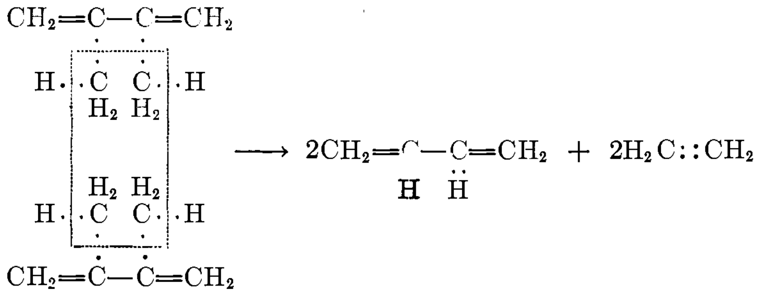
$$2\,CH_2{=}\dot{C}{-}\underset{CH_3}{C}{=}CH_2 \;(H\cdot\,\cdot CH_2) \longrightarrow 2CH_2{=}\underset{H}{\ddot{C}}{-}\underset{CH_2}{C}{=}CH_2 + H_2C{::}CH_2$$

$$2CH_2{=}\underset{H}{\ddot{C}}{-}\underset{CH_3}{\dot{C}}{=}CH_2$$



$$2\,CH_2{=}\dot{C}{-}CH{=}CH_2 \;(H\cdot\,\cdot CH_2) \longrightarrow 2CH_2{=}\underset{H}{\ddot{C}}{-}CH{=}CH_2 + H_2C{::}CH_2$$

(C)



The processes A, B, and C are equally endothermic, though quite dissimilar from the viewpoint of probability of reaction. Processes A and C would require the presence of *cis* molecules, whereas process B would operate on either *cis* or *trans* forms. Process A represents an almost unknown type of reaction. In process B, competitive reactions might greatly reduce the yield of butadiene. The simultaneous tetrademethylenation between two molecules, process C, seems practically excluded on the basis of a preferential didemethylenation between two molecules, yielding 2-methylbutadiene-1,3.

4. Alkynes

Ethyne produces an interesting mixture of hydrogen, methane, ethane, ethene, propene, propadiene, butadiene, ethyne, propyne, benzene, toluene, and napththalene when passed at 420–430°C. over a zinc chloride on pumice catalyst (100). Exposure of ethyne, with or without ethene, to a high-frequency corona discharge results in a slight formation of butadiene (4). The investigators of the last reaction have proposed the following mechanisms in explanation (e' is an activating particle):

In the absence of ethene:

$$CH{\equiv}CH + e' \longrightarrow CH{\equiv}\underset{|}{C} + H + e$$

$$CH{\equiv}CH + H \longrightarrow CH{\equiv}\underset{|}{C} + H_2$$

$$CH{\equiv}\underset{|}{C} + HC{\equiv}CH \longrightarrow CH{\equiv}C{-}CH{=}\underset{|}{C}H$$

$$CH{\equiv}C{-}CH{=}\underset{|}{C}H + H_2 \longrightarrow CH{\equiv}C{-}CH{=}CH_2 + H$$

$$CH{\equiv}C{-}CH{=}CH_2 + H \longrightarrow CH_2{=}\underset{|}{C}{-}CH{=}CH_2$$

$$CH_2{=}\underset{|}{C}{-}CH{=}CH_2 + H_2 \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + H$$

In the presence of ethene:

$$CH{\equiv}CH + e' \longrightarrow CH{\equiv}\underset{|}{C} + H + e$$

$$CH_2{=}CH_2 + H \longrightarrow CH_2{=}\underset{|}{C}H + H_2$$

$$CH_2{=}\underset{|}{C}H + CH{\equiv}CH \longrightarrow CH_2{=}CH{-}CH{=}\underset{|}{C}H$$

$$CH_2{=}CH{-}CH{=}\underset{|}{C}H + H_2 \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + H$$

In the first scheme, butenyne assumes the rôle of an intermediate, while hydrogen is obtained through the cracking of ethyne. The second group of equations was considered to be complementary to the three types of chain reactions, already discussed, pertaining to the conversion of ethene by exposure to the high-frequency discharge (5).

A union of ethene-1,2-diyls ($\dot{C}H{=}\dot{C}H$) with available atomic hydrogens, followed by association of the ensuing free vinyl radicals, is favored by the present authors in lieu of the first chain-reaction scheme:

$$CH{\equiv}CH \rightleftarrows \dot{C}H{=}\dot{C}H$$

$$\dot{C}H{=}\dot{C}H + \dot{H} \rightarrow CH_2{=}\dot{C}H$$

$$2CH_2{=}\dot{C}H \rightarrow CH_2{=}CH{:}CH{=}CH_2$$

Less favored than the present set of reactions, though more acceptable than the chain-reaction mechanism, is the association of ethene-1,2-diyls ($\dot{C}H{=}\dot{C}H$) to form buta-1,3-diene-1,4-diyl ($\dot{C}H{=}CHCH{=}\dot{C}H$), followed by union of the latter with available atomic hydrogens:

$$CH{\equiv}CH \rightleftarrows \dot{C}H{=}\dot{C}H$$

$$2\dot{C}H{=}\dot{C}H \rightarrow \dot{C}H{=}CH{:}CH{=}\dot{C}H$$

$$\dot{C}H{=}CH{:}CH{=}\dot{C}H + 2\dot{H} \rightarrow CH_2{=}CH{:}CH{=}CH_2$$

This mechanism finds support in the formation of thiophene and some butadiene from ethyne at 300–310°C. in the presence of iron pyrites (151).

For the ethene and ethyne juncture, a formation and union of free ethanediyl and ethenediyl radicals is suggested:

$$CH_2{=}CH_2 \rightleftarrows \dot{C}H_2{-}\dot{C}H_2$$

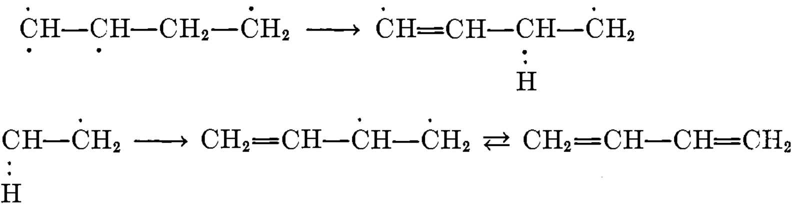
$$CH{\equiv}CH \rightleftarrows \dot{C}H{=}\dot{C}H$$

$$\dot{C}H_2{-}\dot{C}H_2 + \dot{C}H{=}\dot{C}H \rightarrow \dot{C}H_2{-}CH_2{:}CH{=}\dot{C}H$$

The resulting but-1-ene-1,4-diyl upon activation of its double bond, because of the exothermic character of the coupling of C_2 diyls, would form butane-1,1,2,4-tetrayl:

$$\dot{C}H{=}CH{-}CH_2{-}\dot{C}H_2 \rightarrow \underset{\cdot}{\dot{C}}H{-}\underset{\cdot}{C}H{-}CH_2{-}\dot{C}H_2$$

Isomerization would then give but-1-ene-3,4-diyl and covalent butadiene:



$$\underset{\cdot}{\dot{C}}H{-}\underset{\cdot}{C}H{-}CH_2{-}\dot{C}H_2 \longrightarrow \dot{C}H{=}CH{-}\underset{\underset{H}{:}}{C}H{-}\dot{C}H_2$$

$$\dot{C}H{=}CH{-}\underset{\underset{H}{:}}{C}H{-}\dot{C}H_2 \longrightarrow CH_2{=}CH{-}\dot{C}H{-}\dot{C}H_2 \rightleftarrows CH_2{=}CH{-}CH{=}CH_2$$

Ethene and ethyne mixtures are convertible into butadiene also by direct thermal (37, 160) or catalytic (37, 90, 92) methods. However, the De Boistesselin and Dubosc process for the production of artificial rubber first converts the mixture into butyne-1 over animal charcoal at 150°C. and then forms butadiene by isomerizing the product at 300°C. over pumice (22). A catalytic type of interaction between ethyne and ethanol at temperatures above 350°C. is claimed in an old patent application (80). Catalytic dehydration of the ethanol would presumably give ethene, which could then unite with ethyne. The presence of steam would not be inimical unless other components of the catalyst favor hydration of ethyne (9, 110).

Butyne-1 and butyne-2 are readily isomerized to butadiene over catalysts such as magnesium oxide at 460°C. *in vacuo* or in the presence of diluent gases (35). The isomerizations are favored by the exothermic nature of the change of one C—C and one C≡C into two C=C bonds.

5. *Alkenyne*

Butenyne can be hydrogenated to butadiene by contact with (*a*) hydrogen gas and an iron, cobalt, nickel, palladium, or platinum catalyst, (*b*) aqueous solution of chromous sulfate containing free sulfuric acid, or (*c*) zinc dust and solutions of alkaline substances (35). Electrolytic hydrogenation over a platinized electrode is highly selective, not producing butenes simultaneously, contrary to hydrogenations (*a*) catalyzed by Ginzberg's or Paal's palladium, Willstätter's platinum black, Zelinskiĭ and Komarewsky's nickel on alumina catalyst, or (*b*) effected by contact with water and the copper–zinc couple (95). In all these cases, the *desired* hydrogenation probably proceeds by addition of neutral, atomic hydrogen to buta-1,3-diene-1,2-diyl ($\dot{C}H{=}\dot{C}{-}CH{=}CH_2$):

$$CH{\equiv}C{-}CH{=}CH_2 \rightarrow \dot{C}H{=}\dot{C}{-}CH{=}CH_2$$

$$\dot{C}H{=}\dot{C}{-}CH{=}CH_2 + 2\dot{H} \rightarrow CH_2{=}CH{-}CH{=}CH_2$$

The function of Group VIII elements in atomic hydrogenation seems to be "galvanic in nature," with an electron flowing from molecular hydrogen to the metal and from the charged metal to the proton just generated. Close approaches to this mechanism exist in the literature (10, 16, 83). The surfaces of zinc metal and of the copper–zinc couple, like those of the enumerated Group VIII metals, probably temporarily bind and thus conserve atomic hydrogens, but generation of the latter is their principal function.

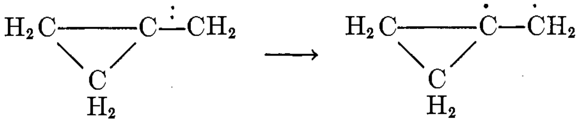
6. Alkadiyne

Butadiyne has been converted into butadiene by contact with (*a*) hydrogen gas in the presence of reduced nickel, platinum, palladium, or copper (11), (*b*) acidified solution of chromous chloride or sulfate (82), or (*c*) zinc dust and sodium hydroxide solution (132). As in the hydrogenation of butenyne, these conversions are probably all dependent upon a supply of neutral hydrogen atoms. Hydrogenation should proceed, therefore, by 1,2 and 1,4 addition, forming butenyne and the unknown butatriene, respectively. The latter would probably immediately isomerize to butenyne or hydrogenate to butadiene. Butenyne from both sources would then undergo its normal hydrogenation to the conjugated alkadiene.

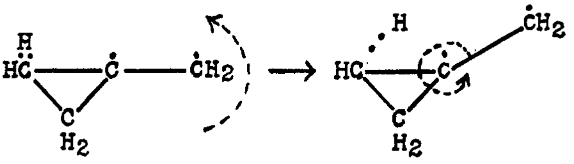
B. CYCLIC SERIES

1. Cyclanes

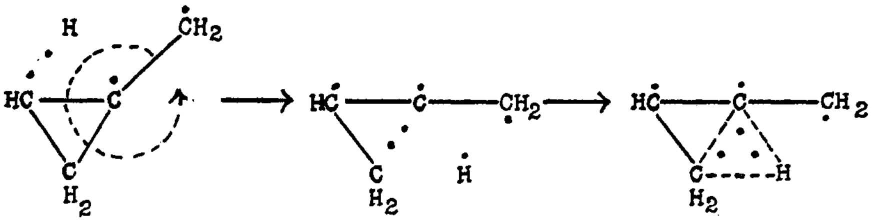
Methylenecyclopropane is converted into butadiene by isomerization at 350°C. over alumina (104). It involves scission of a linkage in the α-position to the double bond, apparently contrary to Schmidt's rule. In formulating the reaction mechanism, *a priori* discussions are obligatory because the ordinary molecular model sets do not contain tetravalent spheres or "carbon atoms" machined for strained rings. We take the primary step to be an activation of the molecule, particularly that of the double bond:



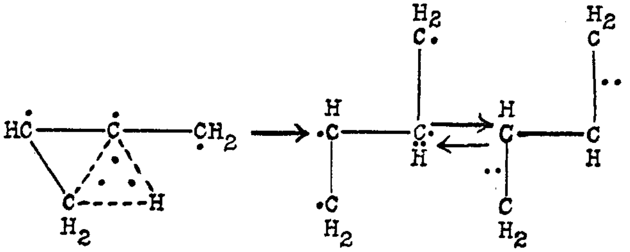
The two π electrons are considered to remain in their activated or open state throughout the conversion into butadiene. Following opening of the double bond, a loosening of a C—H linkage at either "ring CH_2" group is postulated, being incited by proximity of the free valency on the side chain as the latter rotates about the C—C bond:



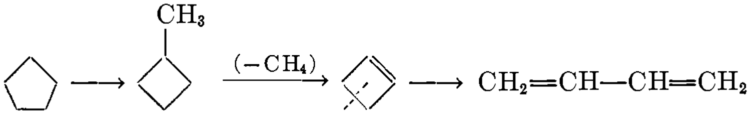
Next, there is projected a scission of the loosened hydrogen atom as it follows the field of the rotating side chain and enters that of the other two carbon atoms, forming an "activated complex:"



The concluding step, whereby *trans*-butadiene is formed, is passage of the complex over a low potential barrier in the direction of this product:

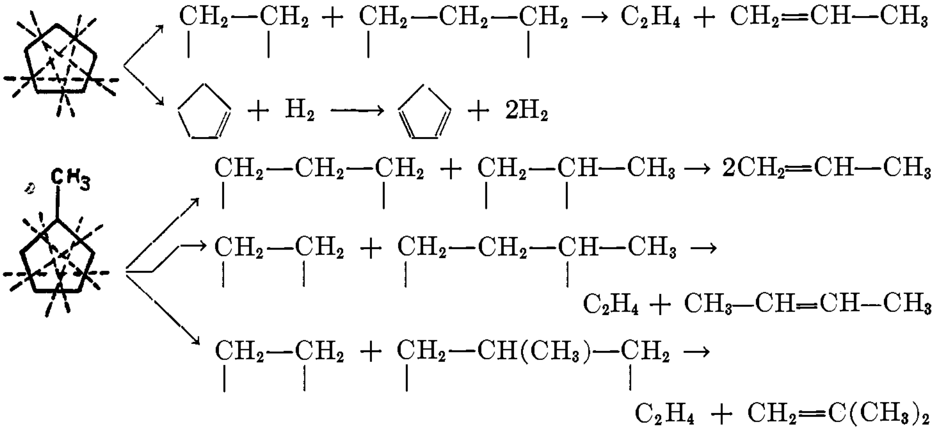


The action of high temperature on methylcyclobutane (120) and cyclopentane (50, 120) results in butadiene formation. Ostromyslenskiĭ explained the cyclopentane conversion as an isomerization to methylcyclobutane, followed by demethanation to cyclobutene and then by β-bond scission (120):



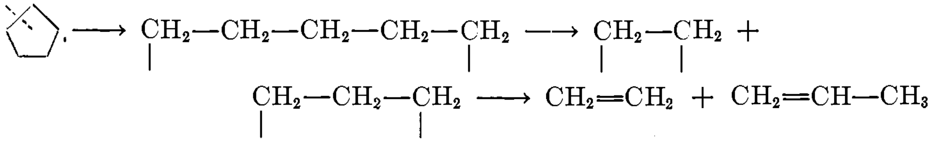
Unfortunately, both cyclopentane and cyclobutene remain unisomerized to date (41). Thermal treatments of methylcyclopentane (50 133) and "dimethylcyclopentane" (50) also yield butadiene.

Lurie (101) considered that thermal decompositions of cyclopentane and methylcyclopentane afford butadiene indirectly through ethene, propene, and, in the case of methylcyclopentane, also *via* butene-2:

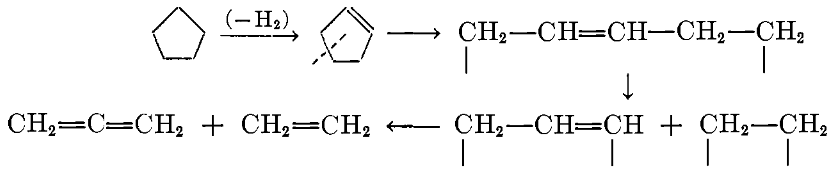


These equations are essentially those of Kazanskiĭ and Platé (87, 88), with the exception of that for butene-2 formation, which was added by Lurie. Kazanskiĭ and Platé failed to find butadiene definitely among the products of the thermal treatment of cyclopentane at 600–800°C. and of methylcyclopentane at 600° or 650°C. Frey's data (53) substantiate the equations just given for the decomposition of cyclopentane.

Rice and Rice postulated an initial formation of pentane-1,5-diyl (i.e., pentamethylene) from cyclopentane (134). Scission of this diyl was considered to give ethene and propene by way of the corresponding diyls:



They also reflected upon the formation of pent-2-ene-1,5-diyl from cyclopentene of dehydrogenation, indicating that its scission would yield ethene and propadiene *via* ethane-1,2-diyl and prop-1-ene-1,3-diyl:



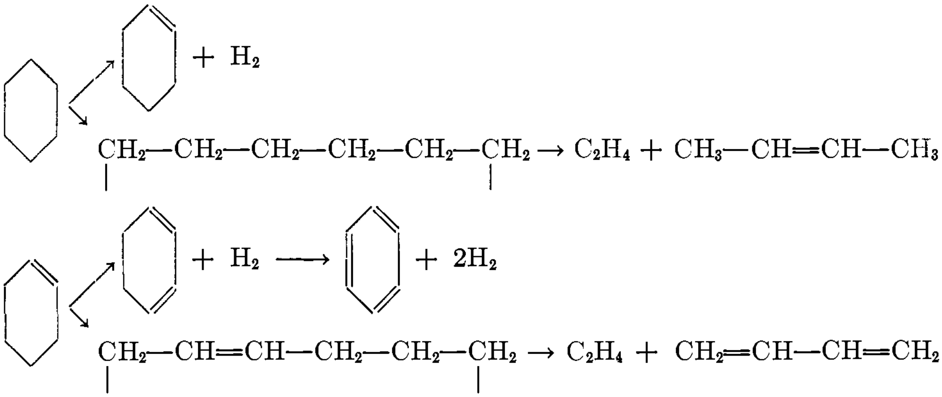
On the contrary, our opinion is that the aforesaid products are those expected from an isomeric diyl, pent-1-ene-1,5-diyl ($\dot{C}H{=}CHCH_2CH_2\dot{C}H_2$), and that pent-2-ene-1,5-diyl should form some butadiene and methylene by a C_4H_6 directive fragmentation:

$$\underset{|}{CH_2}{-}CH{=}CH{-}CH_2{-}\underset{|}{CH_2} \rightarrow \underset{|}{CH_2}{-}CH{=}CH{-}\underset{|}{CH_2} + \overset{|}{\underset{|}{CH_2}}$$

Cyclohexane is convertible into butadiene by thermal treatment at 600–870°C. with 5–36 weight per cent yields per pass (33, 152), or at 539°C. with 12 min. contact time (93), or by catalysis over calcium oxide at 680°C. (81). High pressures are inimical toward the thermal or catalytic conversion (62). The primary reaction in thermal conversion is commonly regarded as dehydrogenation to cyclohexene (84, 88). This cyclene is generally considered to be the common precursor of butadiene and benzene. Pease and Morton first observed a well-marked induction period in the thermal conversion, which delay they ascribed to a slow isomerization, a chain reaction, or a close balance between dissociation and polymerization (129). Data on the established isomerization of cyclohexane into methylcyclopentane indicate that the reaction is endothermic, yielding also dissociation and condensation products (42). This accounts for the observed stasis in pressure measurements.

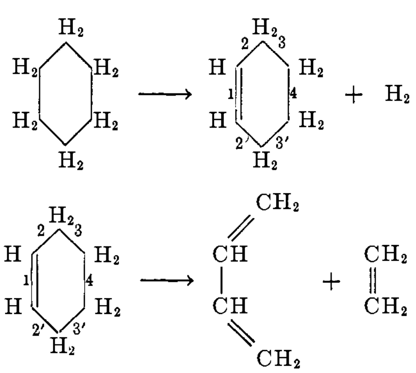
Cyclohexane and methylcyclopentane exist in a state of pseudoequilibrium under conditions yielding butadiene; hence both isomers may participate in its formation. Lurie has discussed the mechanism (*cf. infra*) of butadiene formation from methylcyclopentane (101). It involves scission into ethane-1,2-diyl ($\dot{C}H_2\dot{C}H_2$) and butane-1,3-diyl ($\dot{C}H_2CH_2\dot{C}HCH_3$), conversion of these into ethene and butene-2, respectively, and dehydrogenation of the latter. Of course, under the requisite high-temperature conditions, the excited rather than ground states of methylcyclopentane, ethene, and butene-2 would prevail.

According to Rice and Rice, two primary decomposition mechanisms are possible for cyclohexane (135). Ethene and butene-2, also cyclohexene and hydrogen, are the primary reaction products. Each of these hydrocarbons produces a certain amount of butadiene, but cyclohexene does so in direct competition with aromatization into benzene:

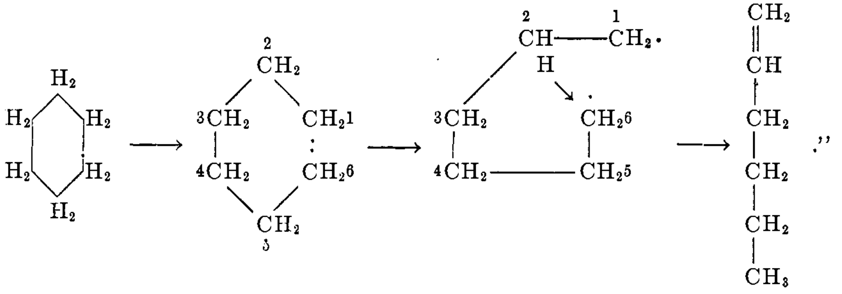


Schmidt considers the mechanism of butadiene formation from cyclohexane to be the following (140):

> "There is no doubt that by cracking cycloparaffins, such as cyclohexane, the greater part of the molecule is first dehydrogenated to tetrahydrobenzene and then split into two fragments, butadiene and ethylene, as I have shown (139). Therefore the series of reactions with primary dehydrogenation and scission on the weak positions 3 and 3′ is experimentally well founded.

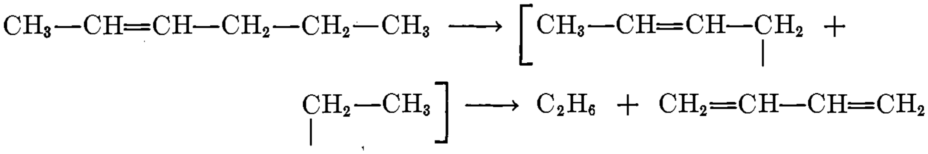


". . . As we have seen, in most of the molecules two C—H bonds are broken and tetrahydrobenzene is formed, which then gives butadiene and ethylene; but a small part of cyclohexane first gives α-hexylene and a carbon bond is broken according to the scheme:

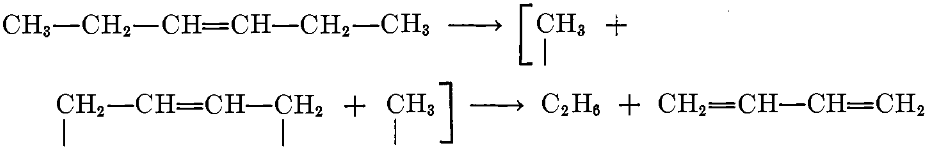


I II III IV ."

Schmidt's hypothesis that butadiene comes exclusively from cyclohexene (i.e., tetrahydrobenzene) appears too restricted. One may presume that sufficient activation of any two adjacent (*ortho* position) hydrogen atoms of cyclohexane would furnish an activated state of the molecule having weakened β-bonds. Upon scission of the mutual β-bond, giving hexane-1,6-diyl ($CH_2CH_2CH_2\dot{C}H_2$-$\dot{C}H_2CH_2$), there would appear hexene-1, hexene-2, and hexene-3 as interconvertible isomers. The last two isomers presumably would obey the double-bond rule, yielding ethane and butadiene:



$$CH_3{-}CH{=}CH{-}CH_2{-}CH_2{-}CH_3 \longrightarrow \left[CH_3{-}CH{=}CH{-}\underset{|}{C}H_2 + \underset{|}{C}H_2{-}CH_3\right] \longrightarrow C_2H_6 + CH_2{=}CH{-}CH{=}CH_2$$



$$CH_3{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_3 \longrightarrow \left[\underset{|}{C}H_3 + \underset{|}{C}H_2{-}CH{=}CH{-}\underset{|}{C}H_2 + \underset{|}{C}H_3\right] \longrightarrow C_2H_6 + CH_2{=}CH{-}CH{=}CH_2$$

At high temperatures, cyclohexane probably undergoes a C_2H_4 directive fragmentation ("depolymerization" to ethene and butene, or ethene exclusively), beginning with the formation of hexane-1,6-diyl. Butadiene would then result from the dehydrogenation of the butenes and the association of vinyl radicals traceable to ethene. Butenes (-1 and -2) for dehydrogenation could also result from the polymerization of ethene.

Methylcyclohexane and "dimethylcyclohexanes" produce butadiene upon contact with hot surfaces, such as electrically heated aluminum silicates (66). Passage of methylcyclohexane or ethylcyclohexane through a quartz tube at 700–

750°C. in the presence of steam forms butadiene in considerable amounts (165).

Two over-all equations can be given for the conversion of methylcyclohexane:

$$C_7H_{14} \rightarrow C_4H_6 + CH_4 + C_2H_4$$

$$2C_7H_{14} \rightarrow 2C_4H_6 + 2C_2H_6 + C_2H_4$$

The first equation corresponds to a demethanation into cyclohexene, which is a less endothermic reaction than dehydrogenation to a methylcyclohexene. Demethanation probably involves two steps of decomposition:

$$C_7H_{14} \rightarrow \dot{C}_6H_{11} + \dot{C}H_3$$

$$\dot{C}_6H_{11} \rightarrow C_6H_{10} + \dot{H}$$

$$\dot{C}H_3 + \dot{H} \rightarrow CH_4$$

The second over-all equation corresponds to the main products when steam is used to facilitate formation of butadiene. Evidently, the last condition favors a greater mingling of free radicals, with the result that atomic hydrogen combines with ethane-1,2-diyl rather than methyl:

$$\begin{array}{l} 2C_7H_{14} \longrightarrow 2C_6H_{10} + 2\dot{C}H_3 + 2\dot{H} \\ 2\dot{C}H_3 \longrightarrow H_3C{:}CH_3 \\ 2C_6H_{10} \longrightarrow 2C_4H_6 + 2\dot{C}H_2\text{—}\dot{C}H_2 \\ \dot{C}H_2\text{—}\dot{C}H_2 + 2\dot{H} \longrightarrow CH_3\text{—}CH_3 \\ \dot{C}H_2\text{—}\dot{C}H_2 \rightleftarrows CH_2{=}CH_2 \\ \hline 2C_7H_{14} \longrightarrow 2C_4H_6 + 2C_2H_6 + C_2H_4 \end{array}$$

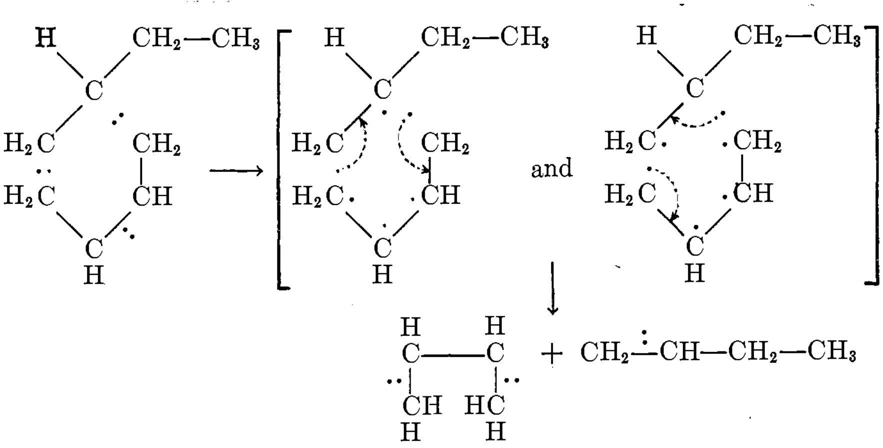
The absolute pressure in the work with steam was probably 0.1 atmosphere, which would aid in the distribution of free radicals.

Ethylcyclohexane probably forms butadiene according to the two equations:

$$C_8H_{16} \rightarrow CH_2{=}CH\text{—}CH{=}CH_2 + CH_2{=}CH\text{—}CH_2\text{—}CH_3 + H_2$$

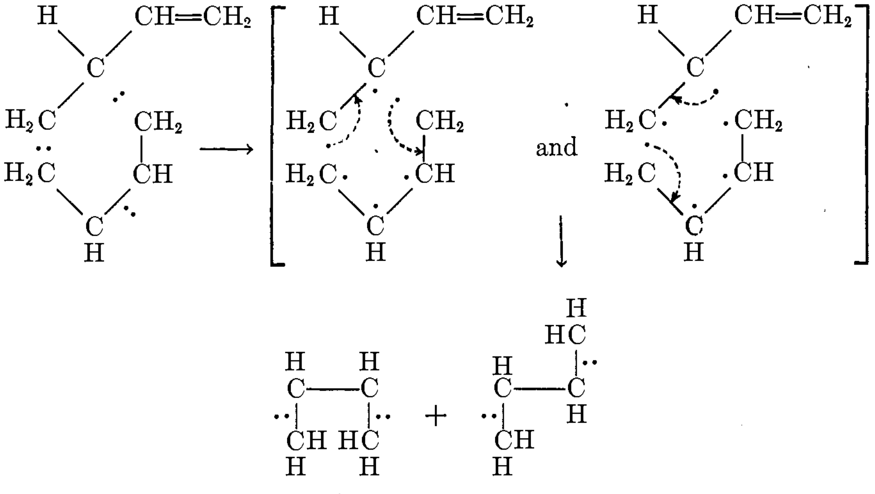
$$C_8H_{16} \rightarrow 2CH_2{=}CH\text{—}CH{=}CH_2 + 2H_2$$

In the first equation, the assumption is made that ring dehydrogenation precedes ring scission, as is probable in the conversion of cyclohexane. 1-Ethylcyclohexene-3 of dehydrogenation would undergo a C_4H_6 directive fragmentation, forming butadiene and butene-1:



cis-Butadiene-1,3 Butene-1

If the butene-1 undergoes 3,4 dehydrogenation, then the first over-all equation gives way to the second, as also occurs when 1-vinylcyclohexene-3 forms from 1-ethylcyclohexene-3:



cis *trans*

In the preceding equation, a formation of *cis*-butadiene from ring atoms in 2-, 3-, 4-, and 5-positions and of the *trans* form from all atoms in 1- and 6-positions of the ring is intended. As these products cool, more *trans* form develops by isomerization. A *trans* configuration for the vinyl group with respect to ring atoms 1 and 6 is specified because of steric interference (repulsion) between the ring-closest *gem* hydrogen atom of the vinyl group and one or the other of the hydrogen atoms in ring position 6, depending on which of the two possible orientations prevails for the 1,6 ring atoms with respect to the common plane of the remaining ring atoms.

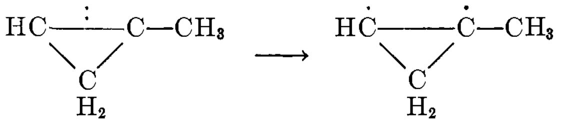
The viewpoint that the second over-all equation is possible follows in part from the facts that 1-vinylcyclohexene-3 is the cyclic dimer (94, 97, 98, 99) of butadiene and that it readily depolymerizes (166) at 500–600°C. The endothermic heat of decomposition of 1-vinylcyclohexene-3 is 23 kcal. per converted gram-mole (48). Dehydrogenation of ethylcyclohexane or ethylcyclohexene is also endothermic. Since these energy requirements are additive, it is evident that the first over-all reaction is most probable:

$$C_8H_{16} \rightarrow C_4H_6 + C_4H_8 + H_2$$

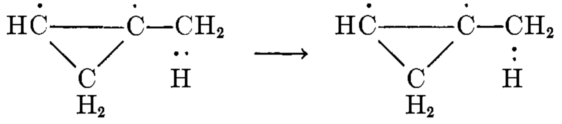
Allylcyclohexane upon thermal treatment yields a trace of butadiene among a great preponderance of decomposition products (73). It does not appear to be convertible in a direct manner.

2. Cyclenes

1-Methylcyclopropene-1 forms butadiene when isomerized at 325°C. over alumina (105). In formulating the reaction mechanism, a decision must be made between scission of the C=C bond to give a C—C linkage and that of a C—H bond in the methyl group as the primary act following an activation of the molecule by the catalyst. The energy expenditure is least in the first process, which leads to the equation:

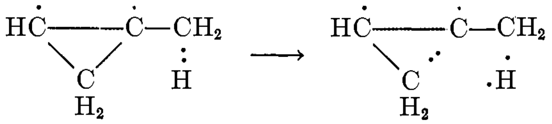


With release of the two electrons, a simultaneous enlargement or slight stabilization of the ring system must occur, owing to the greater length of C—C as compared to C=C bonds (128). Following these two changes, the loosening of a methyl-group hydrogen atom would occur, as expected from the double-bond rule of Schmidt:

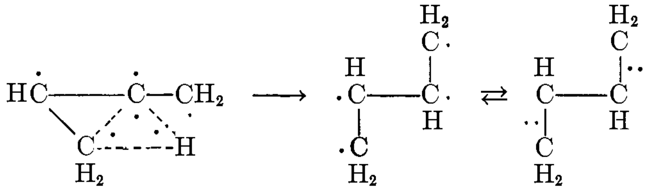


Activation of the double bond does not detract from the applicability of the rule, since β-bond scission is also concerned with bond angles and distances. An allylic type of hydrogen migration, equivalent to forming an active form of methylenecyclopropane, is not postulated because of the detour from the desirable open-bond state of the two carbon atoms destined to form the middle portion of the butadiene molecule.

The fourth step is taken to be a further loosening of the foregoing C—H bond, by formation of a one-electron bond, presumably with the aid of weak attractive forces between the ring CH_2 group and the lone electron:



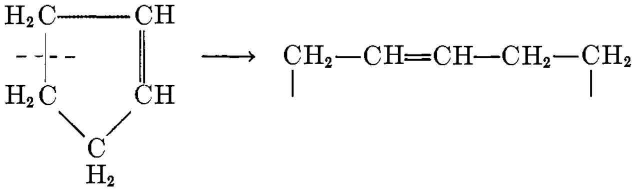
The fifth or final step, which directly forms *trans*-butadiene, is the "reaction" between three atoms in the "transition state:"



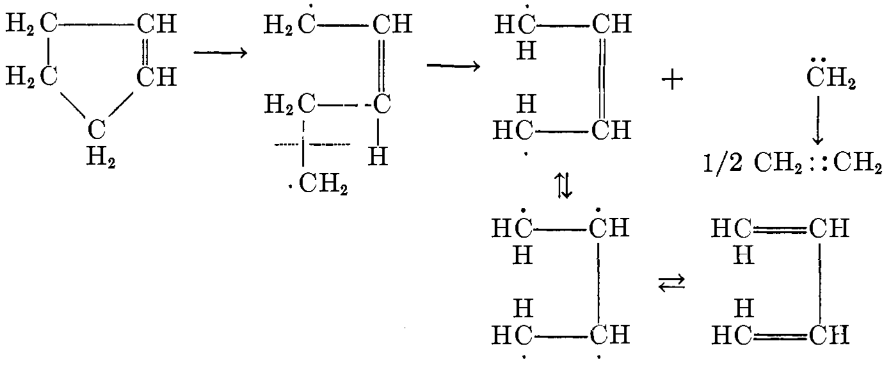
Alumina could facilitate scission of the cyclopropane ring by the formation of a one-electron bond at the ring carbon atom opposite the three-atom complex.

Cyclobutene, an isomer of butadiene, has apparently never been studied from the standpoint of isomerization (43). Reactions (20, 21, 121, 124, 126, 159) in which it is expected as the principal product usually yield the alkadiene, so that thermal and catalytic treatments are expected to give a direct conversion in good yield when polymerization or other side reactions are avoided.

Cyclopentene has been pyrolyzed at 850°C. and 10 mm. mercury absolute pressure, apparently without formation of butadiene or other C_4 products (133). Doubt can be cast upon the reported analyses, because C_2 and C_3 unsaturated aliphatic products were present in considerable quantities. The present writers, however, agree with the explanation given for side courses of the reaction: namely, the formation of pent-2-ene-1,5-diyl instead of cyclopentadiene:



The viewpoint of the investigators was that of the "principle of least motion," postulating minimum motion of the atoms in passing from the starting to the final configurations of nuclei, and also least change of electronic configurations in the reacting system (137). Our viewpoint requires a second application of Schmidt's double-bond rule. Some but-2-ene-1,4-diyl $(\dot{C}H_2CH{=}C\dot{C}H_2)$ plus methylene should develop by scission of the C—C bond in the 4,5-position. Such butenediyl radicals would immediately form covalent butadiene. Under favorable reaction conditions, therefore, the "conversion" of cyclopentene is expected to take the following course:



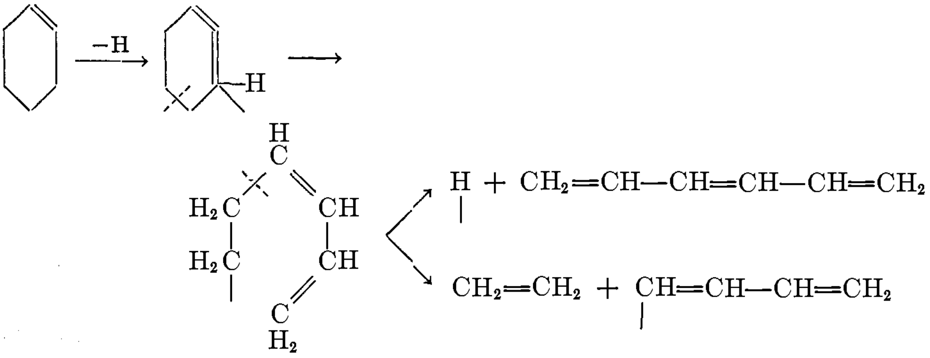
An elimination of methylene would be expected on account of proximity of the hydrogens in the 3- and 5-positions of pent-2-ene-1,5-diyl. The repulsive force set up would be aided by any interaction of 5-position lone electrons with approaching pentenediyls. Scission of methylene followed by coupling to form ethene is indicated on thermodynamic grounds also, i.e., the over-all process would be almost thermoneutral. The ethene so produced would be another, though herein minor, source of butadiene.

The conversion of cyclohexene into ethene plus butadiene has been studied extensively. Thermal treatment affords nearly 50 weight per cent of the alkadiene (34, 89). Low-pressure conditions should favor the reaction by preventing secondary changes and by overcoming an incidental formation of benzene (93, 136). Catalytic processes are available also. Calcium oxide (77), a mixture (78) of magnesium oxide with less than 5 per cent of calcium oxide, and magnesium oxide alone (81) are recommended for use as catalysts at 625°, 650°, and 680°C., respectively. According to Mailhe, the action of silica gel at 550–750°C. on cyclohexene gives a mixture of alkanes, alkenes, and aromatics (102, 103). Formation of pentadiene-1,3 was claimed for the 600° and 650°C. tests, but this may have been confused with that of butadiene because of the proximity in the melting points of 1,2,3,4-tetrabromobutane (m.p. 118°C.) and 1,2,3,4-tetrabromopentane (m.p. 114°C.). Again, the presence of tetrabromobutane may have been masked by a preponderance of the tetrabromopentane, assuming that alkylation conditions converted considerable butadiene into pentadiene-1,3, just as they alkylated the by-product benzene into toluene and *m*-xylene.

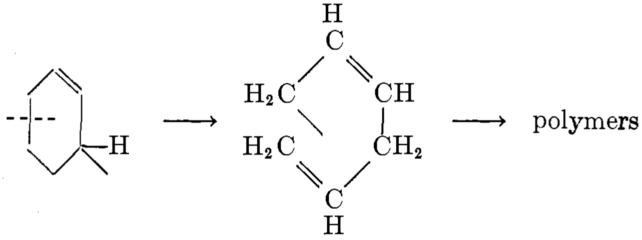
Rice and coworkers (136) assume that the primary step consists of a C—C bond rupture in the β-position to the double bond, in a manner analogous to the scission of alkenes (26, 70, 139, 140, 141), forming a resonating radical that decomposes immediately into ethene and butadiene.

Hurd has suggested that thermal reactions of cyclic hydrocarbons are probably analogous to the chain reactions applied to alkanes, i.e., the chains are perpetuated by some radical (71). Cyclohexene, upon loss of a 3-position hydrogen atom followed by γ-bond scission between carbon atoms 4 and 5, would accordingly form hexa-1,3-dien-6-yl ($CH_2{=}CHCH{=}CHCH_2CH_2{—}$).

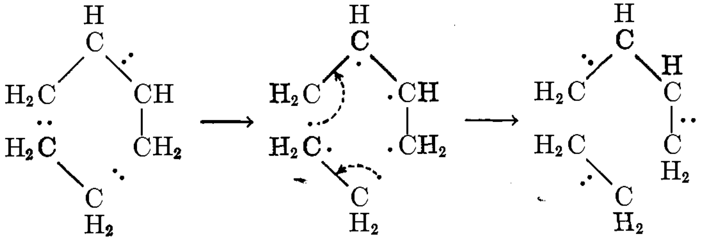
Further conversion, not following Schmidt's double-bond rule, would give a hydrogen atom plus hexatriene-1,3,5 or else ethene and buta-1,3-dien-1-yl:



Union of butadienyl and a hydrogen atom would yield butadiene. Scission of cyclohex-1-en-3-yl between carbon atoms 5 and 6, in the conventional β-bond manner, was considered to give hexa-1,4-dien-6-yl ($CH_2=CHCH_2CH=CH-CH_2-$) and eventually polymers, rather than the now expected butadiene:

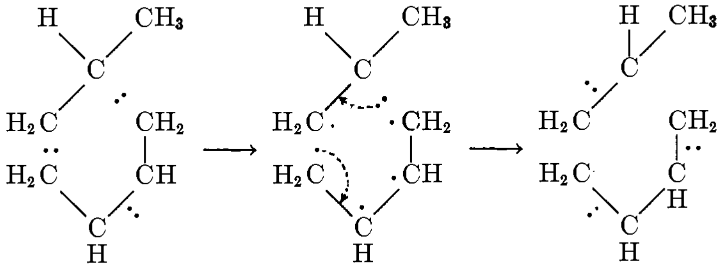


The present writers suggest that cyclohexene probably forms some ethene and *cis*-butadiene in one step by a mechanical twisting-off of ethane-1,2-diyl (construct molecular model!) and redistribution of the four electrons in 3,4 and 5,6 bond positions. The initial, intermediary, and final electronic configurations corresponding to this suggestion are:

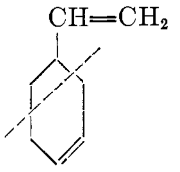


1-Methylcyclohexene-1 yields much ethene and 2-methylbutadiene-1,3 but less than 1 per cent of butadiene when heated at 650–690°C. under partial vacuum conditions (165). This fact fortifies the view that Schmidt's double-bond rule is well operative in the cyclohexene series. The small formation of butadiene can be ascribed to the decomposition of its 2-methyl derivative or to the condensation of ethene under dehydrogenation conditions.

1-Methylcyclohexene-3, as expected, yields much propene plus butadiene when passed through a quartz tube at 690°C. in the presence of steam and under partial vacuum conditions (165):

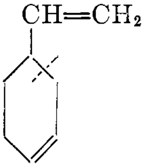


The conversion of 1-vinylcyclohexene-3 into butadiene was regarded by Ostromyslenskiĭ as a true depolymerization, corresponding to that of cyclic terpenes (124, 125):



$$\longrightarrow 2CH_2{=}CH{-}CH{=}CH_2$$

This conception of the over-all reaction prevails to date. A C_4H_6 directive fragmentation explaining the conversion in one step has already been given (see ethylcyclohexane). An alternate explanation having two steps is ring scission between carbon atoms 1 and 2, enhanced because of the critical location of the C—C link being ruptured, i.e., in the β-position to both double bonds. The resultant free diradical, octa-1,6-diene-3,8-diyl, would undergo a conversion into two molecules of butadiene:

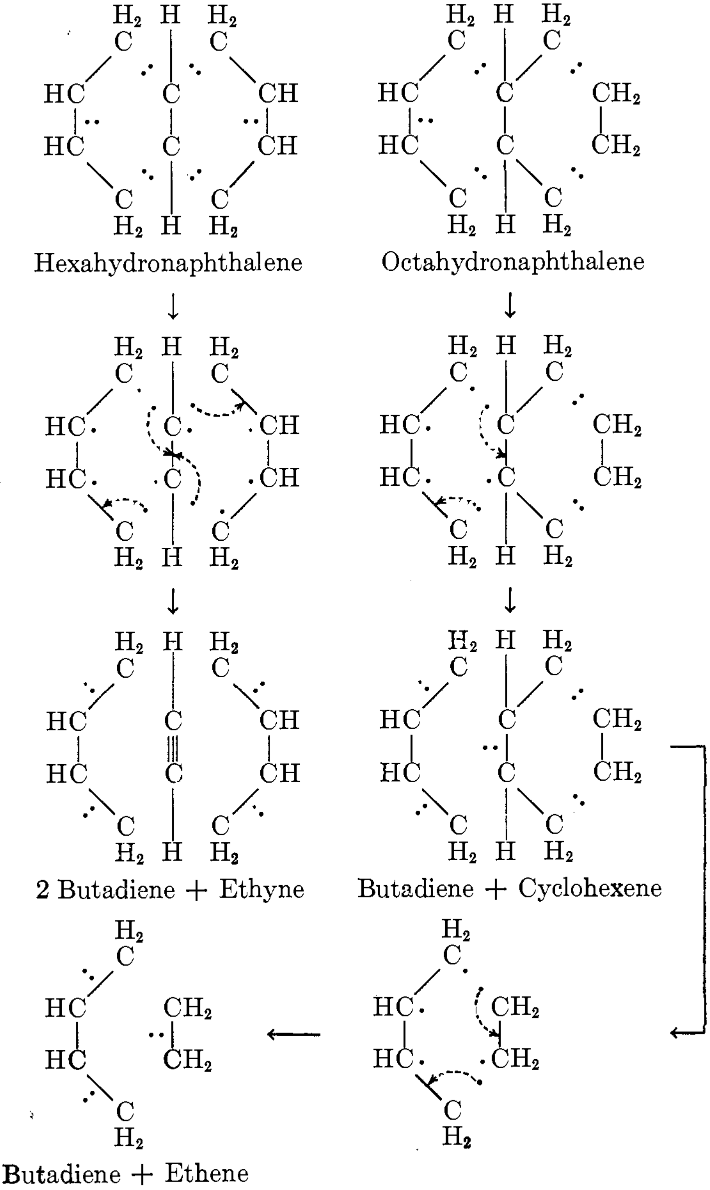


$$\longrightarrow CH_2{=}CH{-}\dot{C}H{-}CH_2{-}\!\!\mid\!\!{-}CH_2{-}CH{=}CH{-}\dot{C}H_2 \longrightarrow 2CH_2{=}CH{-}CH{=}CH_2$$

Splitting occurs only at the 4,5 position in the diyl because its 3-position electron has already satisfied the requirement for β-bond scission with respect to the 1,2 double bond. A butadiene yield of 60 weight per cent is obtainable at 500–600°C. (166).

3. *Bicyclane*

Decahydronaphthalene, i.e., decalin, decomposes at 700–800°C. in the presence of steam to form about 4 weight per cent of butadiene, besides ethene, hydrogen, and other gases (165). The conversion is probably due to several reactions, including condensation of ethene or ethane, through dehydrogenation; ethenylation of ethene by ethyne; dehydrogenation of butane and butenes; chain scission in pentane, hexane, hexenes, and butenylbenzene; and decyclization of cyclohexene, benzene, naphthalene, and tetrahydronaphthalene. These hydrocarbons are among those known to be formed in the thermal treatment of decahydronaphthalene (30). From the viewpoint of Schmidt's double-bond rule, the decyclizations of 1,4,4a,5,8,8a-hexahydronaphthalene and 1,2,3,4,4a,5,8,8a-octahydronaphthalene, i.e., β-octalin, which are possible intermediates, should each give two molecules of butadiene by redistribution of electrons in the 1,8a; 4,4a; 4a,5; 8,8a and 1,2; 3,4; 4a,5; 8,8a bond positions, respectively:



In the case of the conversion of 1,4,4a,5,8,8a-hexahydronaphthalene, a mechanical twisting-off of ethane-1,1,2,2-tetrayl $(\cdot\underset{\cdot}{\mathrm{CH}}\text{—}\underset{\cdot}{\mathrm{CH}}\cdot)$ is suggested by inspection of molecular models. The corresponding torsional removal of cyclohexane-1,2-diyl from 1,2,3,4,4a,5,8,8a-octahydronaphthalene would be competitive with decyclizations to the same cyclanediyl caused by repulsions between hydrogen atoms in the 1-, 2-, 3-, 4-, 4a-, and 8a-positions and those in the 5- and 8-positions, according to the following schedule (repulsions are indicated by colon marks):

MODEL	POSITIONS OF OPPOSING HYDROGEN ATOMS
1	1:8; 4:5. Reverse side shows same numbering.
2	1,1:8,8; 4,4:5,5. Reverse side shows same numbering.
3	1:8; 2:5; 4:5. Reverse side shows 1:8; 3:8; 4:5.
4	1,1:8,8; 4:5; 4a:8. Reverse side shows 1:8; 4,4:5,5; 8a:5.
5	1:5; 1:8; 4:5; 4a:8. Reverse side shows 1:8; 4:5; 4:8; 8a:5.
6	1:8; 2:5; 3:5; 4a:8. Reverse side shows 2:8; 3:8; 4:5; 8a:5.
7	1:8; 2:7; 3:6; 4:5. Reverse side shows same numbering.
8	1:8; 2:8; 3:5; 4:5. Reverse side shows same numbering.
9	1:8; 3:8; 4:5; 8a:5. Reverse side shows 1:8; 2:5; 4:5; 4a:8.
10	1:8,8; 4,4:5,5; 4a:8; 8a:5. Reverse side shows 1,1:8,8; 4:5,5; 4a:8; 8a:5.
11	1,1:8,8; 4,4:5,5; 4a:8; 8a:5. Reverse side shows same numbering.
12	1:5; 1:8; 2:5; 4:5,5; 4a:8. Reverse side shows 1:8,8; 3:8; 4:5; 4:8; 8a:5.
13	1:5; 1:8; 3:5; 4:5; 4a:8. Reverse side shows 1:8; 2:8; 4:5; 4:8; 8a:5.
14	1:5; 1:8; 3:5,5; 4:5; 4a:8. Reverse side shows 1:8; 2:8,8; 4:5; 4:8; 8a:5.
15	1:8,8; 2:8; 4,4:5,5; 4a:8; 8a:5. Reverse side shows 1,1:8,8; 3:5; 4:5,5; 4a:8; 8a:5.

4. Mononuclear aromatic

The formation of butadiene from benzene at high temperatures was studied by Maksimov in Ostromyslenskii's laboratory (117, 124). Dehydrogenation into diphenyl was considered to be the first phase of the reaction. The resultant hydrogen was believed to reduce some benzene into cyclohexane or even hexane. These products, in turn, would give butadiene plus ethene, but the over-all yield was negligible. The equation given was (124):

$$7C_6H_6 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + C_2H_4 + H_2 + 3C_6H_5{-}C_6H_5 \qquad \text{(A)}$$

It should have been written as follows:

$$5C_6H_6 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + C_2H_4 + 2C_6H_5{-}C_6H_5 \qquad \text{(B)}$$

Disproportionation of benzene into diphenyl and cyclohexene was cursorily considered (121). It has the advantage of less hydrogen transfer and consequently greater probability of occurrence:

$$5C_6H_6 \rightarrow C_6H_{10}\ \text{(cyclohexene)} + 2C_6H_5{-}C_6H_5 \qquad \text{(C)}$$

$$7C_6H_6 \rightarrow C_6H_{12}\ \text{(cyclohexane)} + 3C_6H_5{-}C_6H_5 \qquad \text{(D)}$$

$$9C_6H_6 \rightarrow C_6H_{14}\ \text{(hexane)} + 4C_6H_5{-}C_6H_5 \qquad \text{(E)}$$

Because of the regeneration of hydrogen from cyclohexane and hexane in their further transformation into butadiene, equation B still describes the over-all course of conversions proceeding through any of the paths C, D, or E.

Another explanation of benzene conversion is given by the C_4H_6 directive fragmentation theory and, having a constitutional basis, promises greatly increased yields of butadiene as knowledge of decyclization of benzene increases. An interesting elucidation of benzene, hydroxybenzene, and 1,2-dihydroxybenzene conversions (32, 36) centers on the hypothetical elimination of unstable C_2 fragments:

$$C_6H_6 \longrightarrow \dot{C}H_2\text{—}\dot{C}H\text{—}\dot{C}H\text{—}\dot{C}H_2 + \cdot\underset{\cdot}{\dot{C}}\text{—}\underset{\cdot}{\dot{C}}\cdot$$

$$\text{(i.e., } CH_2{=}CH\text{—}CH{=}CH_2 + C{\equiv}C \text{ [or carbon lattice])}$$

$$C_6H_5OH \longrightarrow \dot{C}H_2\text{—}\dot{C}H\text{—}\dot{C}H\text{—}\dot{C}H_2 + \cdot\underset{\cdot}{\dot{C}}\cdot\cdot\underset{\cdot}{\dot{C}}{:}\dot{O} \longrightarrow$$

$$\dot{C}H_2\text{—}\dot{C}H\text{—}\dot{C}H\text{—}\dot{C}H_2 + \cdot\underset{\cdot}{\dot{C}}\cdot + {:}C{::}O$$

$$\text{(i.e., } CH_2{=}CH\text{—}CH{=}CH_2 + \frac{1}{2}\,C{\equiv}C \text{ [or carbon lattice]} + CO)$$

$$C_6H_4(OH)_2 \longrightarrow \dot{C}H_2\text{—}\dot{C}H\text{—}\dot{C}H\text{—}\dot{C}H_2 + \dot{O}{:}\underset{\cdot}{\dot{C}}\cdot\cdot\underset{\cdot}{\dot{C}}{:}\dot{O} \longrightarrow$$

$$\dot{C}H_2\text{—}\dot{C}H\text{—}\dot{C}H\text{—}\dot{C}H_2 + 2{:}C{::}O$$

$$\text{(i.e., } CH_2{=}CH\text{—}CH{=}CH_2 + 2CO)$$

III. CONCLUSIONS

According to theoretical formulations presented here by the authors and supported by many reported processes, butadiene can be prepared from all ordinary hydrocarbons. Certain members, such as *n*-butane, ethene, butene-1 or -2, butenyne, butyne-1 or -2, butadiyne, cyclohexane, cyclohexene, and 1-vinylcyclohexene-3, are highly convertible into butadiene. The clue to this behavior is their electronic and molecular structures, which approach those of butadiene. This statement applies also to the activated or momentarily reacting molecules. A deficiency of hydrogen or tendency thereto must be counteracted, as in the case of butenyne or butadiyne. If hydrogen must be removed, as with *n*-butane and the butenes, catalytic dehydrogenation gives superior results compared with thermal treatment. Although it would be desirable to dehydrogenate cyclohexane into cyclohexene prior to final conversion, its catalytic dehydrogenation would yield benzene. Considerable research remains to be carried out on the juncture of ethene with itself or with ethyne to produce butadiene.

Two types of molecular scission, designated as C_2 and C_4 directive fragmentations, probably exist and favor the production of butadiene from individual hydrocarbons. These scissions provide C_2 and C_4 fragments that retain their own hydrogen atoms and conceivably can become stabilized through the formation of butadiene. Schmidt's double-bond rule applies to these fragmentations, but its scope must be extended to permit scission of a C—H bond in the β-position to a double bond.

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