

# UNITED STATES PATENT OFFICE

2,343,830

## PREPARATION OF DIOLEFINS

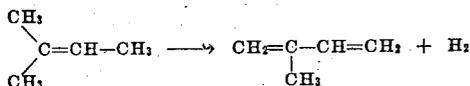
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No Drawing. Application June 26, 1940,  
Serial No. 342,590

8 Claims. (Cl. 260-680)

This invention relates to a method for the preparation of diolefins from pentenes and, more particularly, for the preparation of penta dienes from pentenes.

It has been found that pentenes can be broken down by pyrolytic decomposition to yield penta dienes and other conjugated diolefins by the removal of two atoms of hydrogen. The reaction involved may be illustrated by the following equation for the formation of isoprene from trimethyl ethylene:



Any of the pentenes may be thus treated to form the penta dienes.

The pentenes include the following:

n-Propyl ethylene, $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$ .....	B. P. 39
Pentene-2, $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$ .....	C. 36.4
2-methyl-butene-1, $\text{CH}_3-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$ .....	C. 32

Trimethyl ethylene, $\begin{array}{c} \text{CH}_3 \\   \\ \text{C}=\text{CH}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$ .....	C. 38.4
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Isopropyl ethylene, $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}-\text{CH}=\text{CH}_2 \\   \\ \text{CH}_3 \end{array}$ .....	C. 20.1
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From these various pentenes may be prepared one or more of the following penta dienes:

Isoprene, $\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\   \\ \text{CH}_3 \end{array}$ .....	B. P. 34
Piperylene, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_2$ .....	C. 42
Sym. dimethyl allene, $\text{CH}_3-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2$ .....	C. 49
Penta diene 1:4, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$ .....	C. 29
2-methyl butadiene 2:3, $\begin{array}{c} \text{CH}_3-\text{C}=\text{C}=\text{CH}_2 \\   \\ \text{CH}_3 \end{array}$ .....	C. 41
Ethyl allene, $\text{CH}_2=\text{C}=\text{CH}-\text{C}_2\text{H}_5$ .....	C. 45

Cyclo penta diene, $\begin{array}{c} \text{CH}_2 \\   \\ \text{HC}=\text{C}=\text{CH} \\   \\ \text{CH}-\text{CH} \end{array}$ .....	C. 42.5
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Dicyclo penta diene, $\begin{array}{c} \text{CH} \\   \\ \text{HC}=\text{C}=\text{CH} \\   \quad   \\ \text{CH} \quad \text{CH} \\   \quad   \\ \text{HC} \quad \text{CH}_2 \\   \quad   \\ \text{CH} \quad \text{CH} \end{array}$ .....	mm. 95/55
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Other conjugated diolefins, such as other buta-dienes, may also be obtained.

However, it is not possible merely to subject

the pentenes to a high degree of heat in order to obtain the penta dienes since, as will be observed by inspection of the data given above, the boiling points of the penta dienes do not in general differ from the boiling points of the pentenes by an amount great enough to permit ready separation of the product from unchanged starting material. Particularly is this true of isoprene and trimethyl ethylene. In order to overcome this difficulty of separation, the present invention contemplates pyrolysis of the pentenes to such an extent as to convert all or substantially all of the starting material to other compounds with, of course, as high a proportion of penta dienes in the product as possible. When the pyrolysis is conducted in this manner, there will be no problem of separation of unconverted pentene or pentenes from the penta diene or penta dienes which are desired. This results from the fact that the decomposition products, other than the penta dienes, have boiling points which differ from the boiling points of the penta dienes by a substantial amount, the difference being, on the average, larger than that which separates the boiling points of the pentenes and the penta dienes respectively. Some of these decomposition products are hydrogen, methane, ethylene and propylene, all of which boil much lower than do the five-carbon compounds.

Generally speaking, the pyrolysis may be conducted at a temperature ranging between 700° and 1400° C., the preferred range within which best results are obtained, being 900° and 1100° C. The starting material should be subjected to this temperature for a period between 0.5 and .03 second, but usually the contact time will range between 0.2 and .05 second. The pressure should be less than atmospheric, pressures corresponding to a range of 10-60 mm./Hg having been found practical, but, obviously the pressure as well as temperature and contact time, may be varied somewhat from the limits given depending on the nature of the starting material and the results desired. That is to say, if it is desired to obtain a particular diolefin with clean separation from the other products by pyrolysis, one set of conditions may be employed, whereas if a larger yield of mixed conjugated diolefins is desired, another set of conditions may be more effective.

The method of the invention may also be used to prepare individual pentadienes, such as isoprene from trimethyl ethylene. In general, where it is desired to secure any given pentadiene, it will be found that the branched chain pentenes tend to yield larger quantities of those pentadi-

enes which are likewise characterized by a branched chain. For example, trimethyl ethylene, unsym. methyl ethyl ethylene and isopropyl ethylene may be expected to yield larger quantities of isoprene and of 2-methyl butadiene 2:3, while N-propyl ethylene and sym. methyl ethyl ethylene may be expected to produce larger proportions of piperylene sym. dimethyl allene, penta diene 1:4 and ethyl allene. Of course, no clear cut division can be made since considerable rearrangement occurs in the pyrolysis of these unsaturated compounds and varying amounts of a given diolefin, such as one of the pentadienes mentioned, may be formed from any of the pentenes.

To illustrate the method, the following example is given:

Trimethyl ethylene is passed through a reaction tube which is heated to a temperature between 900-1100° C., the material being drawn through while maintaining a pressure of 30-54 mm. of mercury. The tube used may be either a 3 mm. quartz tube or a standard 1/4" pipe of Allegheny metal. Quartz pellets or other packing material may be placed in the tube so as to adjust the free space to the desired volume. Heat was supplied by a 12" combustion furnace and the reaction tube was placed inside a 7/8" Pythagoras tube. The temperature was measured and a thermocouple placed between the inner and the outer tube in the center of the heated zone. The following results were obtained:

Reaction tube	Temp.	Rate of feed	G. isoprene/100 g. trimethyl ethylene entering
	°C.	G./min.	
Quartz.....	1,100	1.13	25.7 <sup>(1)</sup>
Allegheny metal.....	900	3.65	17.5

The results given above are not strictly comparable since the yield of 25.7 grams obtained in the quartz tube represents all of the conjugated diolefins produced, the analysis being made by the maleic anhydride method. On the other hand, the yield of 17.5 grams obtained in the Allegheny metal tube represents isoprene, the total conjugated diolefins by the maleic anhydride method being 38.5 grams in this instance. By properly adjusting the temperature and rate of flow of trimethyl ethylene, isoprene of 90-95% purity can readily be obtained.

While there has been described above the preferred embodiment of the invention, it will be apparent that the method as outlined may be modified in various particulars without departing from the scope of the invention. The temperature may be varied from the range given depending on the particular pentene which is being pyrolyzed and depending on whether a product is desired which gives little trouble in separating the diolefin from the remaining products. Also, mixtures of pentenes may be pyrolyzed to obtain mixtures of diolefins or mixtures of pentadienes suitable for polymerization.

Accordingly, the invention is not limited by the foregoing disclosure but only by the appended claims in which it is intended to include all features of patentable novelty residing in the invention.

What I claim is:

1. A method of preparing pentadienes which

comprises pyrolyzing a material made up of at least one pentene and containing only pentenes at a temperature between about 900° and 1100° C., and under a pressure corresponding to about 10 to 60 mm./Hg, in the absence of a catalyst, until substantially all of the pentene material has been converted to other substances and then distilling to separate the pentadiene from the other conversion products.

2. A method of preparing pentadienes which comprises pyrolyzing a material made up solely of at least one pentene at a temperature between about 900-1100° C., under a pressure corresponding to about 30 to 60 mm./Hg, in the absence of a catalyst for a period of 0.03 to 0.5 seconds to convert all of the pentene material to other substances having boiling points substantially differing from that of the pentene constituents of the material treated and then distilling to separate the pentadienes from the other conversion products.

3. A method of preparing isoprene which comprises pyrolyzing a material constituted solely by a branched chain pentene at a temperature between about 900° and 1100° C., and under a pressure corresponding to 10 to 60 mm./Hg, in the absence of a catalyst, until substantially all of the pentene has been converted to other substances and then distilling to separate the isoprene.

4. A method of preparing isoprene which comprises pyrolyzing a material constituted solely by a branched chain pentene at a temperature between about 900° and 1100° C., and under a pressure corresponding to about 30 to 60 mm./Hg, in the absence of a catalyst, until substantially all of the pentene has been converted to other substances and then distilling to separate the isoprene.

5. A method of preparing isoprene which comprises pyrolyzing a material constituted solely by a branched chain pentene at a temperature between about 900° and 1100° C. in the absence of a catalyst under a pressure corresponding to between about 10 to 60 mm./Hg until substantially all of the pentene has been converted to other substances and then distilling to separate the isoprene.

6. A method of preparing isoprene which comprises subjecting trimethylethylene to a temperature between about 900° and 1100° C. in the absence of a catalyst under a pressure corresponding to between about 30 to 60 mm./Hg until substantially all of the trimethylethylene has been converted to other substances and then distilling to separate the isoprene.

7. A method of preparing isoprene which comprises subjecting isopropylethylene to a temperature between about 900° and 1100° C. in the absence of a catalyst under a pressure corresponding to between about 30 to 60 mm./Hg until substantially all of the isopropylethylene has been converted to other substances and then distilling to separate the isoprene.

8. A method of preparing isoprene which comprises subjecting unsym. methylethylethylene to a temperature between about 900° and 1100° C. in the absence of a catalyst under a pressure corresponding to between about 30 to 60 mm./Hg until substantially all of the unsym. methylethylethylene has been converted to other substances and then distilling to separate the isoprene.

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