

UNITED STATES PATENT OFFICE.

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PROCESS FOR MAKING HOMOLOGUES OF STYROL FROM AROMATIC HYDROCARBONS.

No Drawing. Original application filed May 7, 1924, Serial No. 711,583. Divided and this application
filed January 30, 1925. Serial No. 5,892.

To all whom it may concern:

Be it known that we, IWAN OSTROMISLENSKY and MORRIS G. SHEPARD, a citizen of Russia and a citizen of the United States, respectively, both residents of New York, county and State of New York, have invented certain new and useful Improvements in Processes for Making Homologues of Styrol from Aromatic Hydrocarbons, of which the following is a full, clear, and exact description.

This invention relates to the production of homologues of styrol by the pyrogenic decomposition of hydrocarbons having nine or more carbon atoms, more than two of which are in the side chain. More particularly it relates to the production of homologues of styrol by splitting off a hydrocarbon group from homologues or analogues of benzol.

This invention is a division of our copending application Serial No. 711,583, filed May 7, 1924.

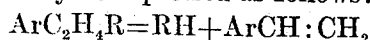
The object of the invention is to provide a process for producing homologues of styrol by heating hydrocarbons having at least ten hydrogen atoms and at least nine carbon atoms, more than two of which are in a side chain to a temperature of approximately 500° C. to approximately 700° C., and partially decomposing the hydrocarbon by the removal of an alkyl group therefrom to form compounds having the general formula ArCH:CH_2 where Ar is aryl.

This case is a continuation in part of our application Serial No. 648,751, filed June 30, 1923.

Briefly the apparatus consists of a source of carbon dioxide or other neutral gas from which the gas is led by a pipe through a flow-meter whence it is introduced into the interior of an iron pipe which is heated to the required temperature by gas burners or other suitable means. Communicating with the iron tube through a suitable valve and sight glass is a container for the hydrocarbon which constitutes the raw material in the process. The temperature is determined for example by means of a thermo-couple, the temperature determination being made on the gas in the interior of the tube at about

the middle. A condenser and receiver are provided and a gas holder is connected therewith to collect uncondensable gases.

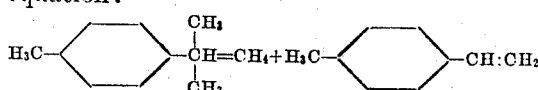
The general reaction involved in this invention may be expressed as follows:



where Ar is aryl and R represents an alkyl radical. In this reaction an alkyl radical is split off.

Depending upon the nature of Ar whether it contains an alkyl group or alkyl groups, such as methyl or ethyl groups or both, will depend the nature of the ArCH:CH_2 produced.

This process has been investigated in connection with cymene. The reaction occurs according to the following equation. Cymene which is known as para methyl iso propyl benzol yields para methyl styrol in the equation:



Specifically the process employing cymene may be carried out as follows: Cymene is introduced from the container into the tube at a rate of .5-.6 grams per minute. The tube is heated to 650° C., the diameter of the tube being 25 cm. and length subjected to heating, 67 cm. A current of carbon dioxide at low pressure is passed through the tube continuously during the whole process. The liquid reaction products condense in the receiver which is water cooled. The methane formed in the reaction may be collected in the gasometer. The product resulting from treatment of cymene in 4 hrs. and 20 mins. was 87 grams of liquid reaction products from 100 grams of cymene. By treating the liquid reaction product with steam 67 grams of crude methyl styrol appeared in the distillate and the remaining 20 grams of liquid products in the distilling flask. An analysis of the distillate showed that it contained 35.5 grams, i. e. 53.2% of paramethylstyrol, the main part of the by-products in this crude methyl styrol being unchanged cymene which is easily regenerated under ordinary conditions. Eliminating the regenerated cymene, consequently the yield of methyl

styrol under the conditions mentioned is 40-50% calculated on the weight of the original cymene taken.

- 5 Cymene may be obtained by transformation of a wide variety of terpenes. In particular it may be obtained from cheap varieties of turpentine which in turn are made by distilling shavings of pine-tree stumps with steam.
- 10 The processes described are simple and economical, and require simple apparatus only. They produce a relatively high yield of the desired product.

- 15 The above example with cymene is representative of a number of reactions which can be carried out with raw materials containing other groups. The nature of the side chain may be varied considerably, as long as the above general reaction of splitting off an alkyl radical will yield a product of the general formula $ArCH:CH_2$. Obviously other positions in the aryl group may be occupied. Mixtures of hydrocarbons falling within the category of this invention
- 20 may be used to form mixtures of styrol homologues in a manner similar to that mentioned in our copending application Serial No. 5891, filed January 30, 1925.

- 25 It will thus be seen that among others the objects of the invention above enumerated are achieved.

- 30 As many apparently widely different embodiments of this invention may be made without departing from the spirit thereof, it will be understood that we do not intend to limit ourselves to the specific embodiment herein set forth except as indicated in the appended claims.

Having thus described our invention, what we claim and desire to protect by Letters Patent is:

1. A process for making compounds of the type $R'ArCH:CH_2$ where Ar represents aryl and R' an alkyl substitution therein, which comprises heating a hydrocarbon having the general formula $R'ArC_2H_4R$ where R represents group substitution in the side chain of said compound, and removing RH therefrom to form a compound of the type $R'ArCH:CH_2$.

2. A process for making a homologue of styrol which comprises heating an alkylated alkyl benzol containing at least three carbon atoms in at least one of the side chains, and splitting sufficient alkyl groups from said side chain to yield a homologue of styrol.

3. A process for making a homologue of styrol which comprises heating an isomer of alkylated iso propyl benzol to a temperature of approximately 500-700° C., and liberating methane from the isopropyl side chain thereof to produce a homologue of styrol.

4. A process for making para methyl styrol which comprises passing a current of vaporized para methyl iso propyl benzol through a tube heated to a temperature of approximately 650° C. and liberating methane from said iso propyl group to produce para methyl styrol.

Signed at Cromwell, Connecticut, this 26th day of January, 1925.

IWAN OSTROMISLENSKY.

Signed at New York, New York, this 28th day of January, 1925.

MORRIS G. SHEPARD.