

UNITED STATES PATENT OFFICE

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PRODUCTION OF ALICYCLIC KETONES
FROM ALICYCLIC ALCOHOLSFriedrich Laucht, Leuna, Germany; vested in the
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7 Claims. (Cl. 260—586)

The present invention relates to the production of alicyclic ketones from alicyclic alcohols.

The preparation of ketones by the catalytic dehydrogenation of secondary alcohols has heretofore been suggested. Thus, vaporized secondary alcohols have been led over copper-zinc alloys, in particular over alloys containing equal amounts of copper and zinc.

In the production of alicyclic ketones with the aid of such catalysts, there is usually observed a too far-reaching dehydrogenation with the formation of phenol and, furthermore, a dehydration with the formation of olefinic bodies. It is very difficult to free alicyclic ketones from phenols. The distillation in the presence of alkali metal hydroxides, which would keep back the phenols, cannot be carried out, because the ketones undergo intermolecular condensations in the presence of alkali metal hydroxides. It is also very difficult to wash out the phenols with dilute alkali metal hydroxide solutions because of the high density of alicyclic ketones. Cyclohexanone may be, it is true, separated from phenol by rectification. This process, however, involves additional expenses; it cannot be used at all when purifying mixtures of cyclohexanone and its homologues because of the overlapping of the boiling points of the ketones with those of the phenols.

It is an object of the present invention to produce alicyclic ketones which are free from phenolic bodies and free from substantial amounts of olefines by carrying out the dehydrogenation at temperatures not substantially exceeding 500° C. with the aid of zinc alone or of zinc containing up to 20 per cent of copper, preferably not more than 15 per cent of copper. According to the present invention there may be used as catalyst zinc alone or zinc being admixed or alloyed with small amounts of copper amounting up to 20 per cent. Small amounts of other ingredients usually to be found in the commercial grades of zinc do not prevent the satisfactory operation of the process.

The invention may be used in the dehydrogenation of monocyclic alicyclic alcohols, such as cyclohexanol and its homologues and mixtures thereof, as they are obtained in the hydrogenation of monocyclic phenols, as well as in that of other alicyclic alcohols, e. g. of decahydronaphthol. The catalysts are used in such a form as to offer a large surface to the gaseous alcohol, while care is taken that the flow of the gases is not hindered. Preferably, the catalysts are

used in the form of netting, rolled-up netting, spirals, threads or cuttings.

The vaporized alcohols may be led over the catalyst together with inert diluent gases, as for example with nitrogen, hydrogen or steam. It is preferable to work at normal pressure; however, the process may also be carried out under sub-atmospheric or superatmospheric pressure.

The most favorable reaction temperature depends on the catalyst. Generally speaking, the most favorable reaction temperature may be increased within the range of from about 380 to 500° C. with increasing copper content. While temperatures from about 380 to 390° C. are most favorable in the use of zinc alone, the optimal temperature amounts to about 420° C. for a copper content of 5 per cent, to about 440° C. for a copper content of 10 per cent, and to from about 460 to 480° C. for a copper content of 15 per cent. Other temperatures within the range of from 380° to 500° C. may be used for the various catalysts set forth above without the formation of undesirable by-products, the rate of conversion being somewhat poorer.

Furthermore, it is preferable to avoid temperatures above the melting point of the catalysts because otherwise the surface offered to the alcohol vapors becomes small. When working below 380° C., the rate of conversion decreases, in other words mixtures of alcohols and ketones are obtained which are useful for many technical purposes. Working below 300° C. is no longer economical due to the very slow speed of conversion.

The following examples will serve to illustrate the nature of this invention. It is, however, not restricted to these examples.

Example 1

1 kilogram of vaporized cyclohexanol per hour is led at 440° C. through a tube made from V2A steel of 2 meters length and 36 millimeters internal diameter which is charged with 1.5 kilograms of turnings of an alloy consisting of 90 per cent of zinc and 10 per cent of copper. The vapors emerging from the tube are condensed. The condensate contains from 90 to 95 per cent of cyclohexanone, less than 1 per cent of cyclohexene, the balance consisting of unchanged cyclohexanol.

Example 2

15 grams of vaporized methylcyclohexanol (obtained by hydrogenation of a mixture of iso-

meric cresols) per hour are led at 420° C. through a glass tube of 80 centimeters length and 20 millimeters internal diameter charged with 40 grams of turnings of an alloy containing 95 per cent of zinc and 5 per cent of copper. By condensing the vapors emerging from the tube a liquid is obtained consisting of from 85 to 90 per cent of methylcyclohexanone, unchanged methylcyclohexanol and less than 1 per cent of methylcyclohexene.

Example 3

1 kilogram of a mixture of 40 per cent of cyclohexanol, 40 per cent of methylcyclohexanol and 20 per cent of dimethylcyclohexanol (obtained by hydrogenating a mixture of phenol, cresols and xlenols) is led per hour at about 390° C. through a tube as described in Example 1 which is charged with 1 kilogram of zinc turnings. By condensing the vapors emerging from the tube, a mixture is obtained which contains from 85 to 90 per cent of alicyclic ketones, unchanged alicyclic alcohols and less than 1 per cent of cyclic olefines.

What I claim is:

1. A process for the production of alicyclic ketones by catalytic dehydrogenation of alicyclic alcohols which consists in leading vaporized alicyclic alcohols containing at least 6 carbon atoms at temperatures between 300 and 500° C. over a metallic body selected from the group consisting of zinc and zinc containing up to 20 per cent of copper.

2. A process for the production of alicyclic ketones by catalytic dehydrogenation of alicyclic alcohols which consists in leading vaporized alicyclic alcohols containing at least 6 carbon atoms

at temperatures between 380 and 500° C. over a metallic body selected from the group consisting of zinc and zinc containing up to 20 per cent of copper.

3. A process for the production of alicyclic ketones by catalytic dehydrogenation of alicyclic alcohols which consists in leading vaporized monocyclic alicyclic alcohols containing at least 6 carbon atoms at temperatures between 380 and 500° C. over a metallic body selected from the group consisting of zinc and zinc containing up to 20 per cent of copper.

4. A process for the production of alicyclic ketones by catalytic dehydrogenation of alicyclic alcohols which consists in leading vaporized alicyclic alcohols containing at least 6 carbon atoms at temperatures between 300 and 500° C. over zinc containing up to 15 per cent of copper.

5. A process for the production of alicyclic ketones by catalytic dehydrogenation of alicyclic alcohols which consists in leading vaporized cyclohexanol at temperatures between 380 and 500° C. over zinc containing up to 15 per cent of copper.

6. A process for the production of alicyclic ketones by catalytic dehydrogenation of alicyclic alcohols which consists in leading vaporized methylcyclohexanol at temperatures between 380 and 500° C. over zinc containing up to 15 per cent of copper.

7. A process for the production of alicyclic ketones by catalytic dehydrogenation of alicyclic alcohols which consists in leading vaporized dimethylcyclohexanol at temperatures between 380 and 500° C. over zinc containing up to 15 per cent of copper.

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