

Camphor and its Industrial Synthesis

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Abstract:

A brief historical review of synthetic camphor technology is presented together with chemical description for each of specific stage of the process. An input of Russian chemists into elaboration of industrially accessible methods of camphor production is discussed.

Camphor, 1,7,7-trimethylbicyclo[2.2.1]heptane (**Scheme 1**, compound I), is a ketone related to bicyclic terpenoids which was already known in ancient times. It was used in a medicine, as a repellent, in cooking and in religious ceremonies. Camphor possesses a strong aromatic odor and forms colorless crystals (m.p. 178-179 °C), which are well soluble in ethanol and many other organic solvents and only slightly in water. By chemical properties camphor represents typical ketone, thus it is reduced to two stereoisomeric alcohols – borneol and isoborneol. Camphor has two asymmetric carbon atoms and due to its chirality exists as two stereoisomers (-)-camphor and (+)-camphor.

Natural camphor is produced from camphor tree (*Cinnamomum camphora*) which is native to South China, Taiwan and Japan. One of the important properties of camphor is its ability to undergo steam distillation. Wood and foliage of camphor tree at first were chipped and then subjected to steam distillation. Crude camphor separated as a solid matter after cooling with the yield of about 1%. Final purification of camphor is achieved by single or double sublimation of crude camphor or by recrystallization.

In 1870 a horn-like mixture of nitrocellulose and camphor was invented by brothers John and Isaiah Hyatt. The material which received trademark celluloid began to be used in production of photography films, buttons, dressing table sets, dolls and many other applications. It is noteworthy to mention here the recent publication in which carbon nanotubes were successfully synthesized from camphor [2].

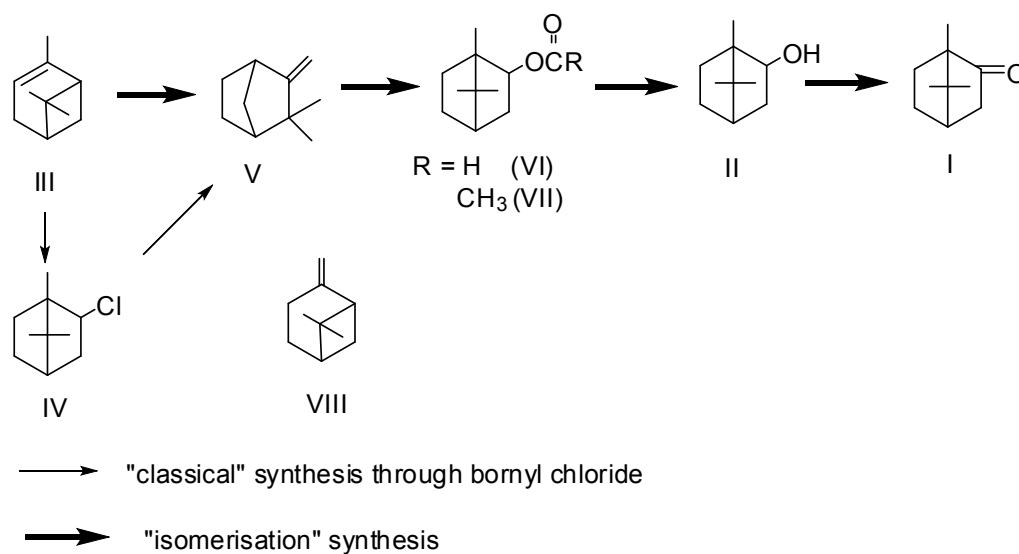
Another important consumer of camphor became the production of smokeless gunpowder where the addition of camphor reduces the gunpowder liability to spontaneous explosion. All these industrial demands substantially increase the camphor consumption at the beginning of 20th century and raise the natural camphor price. The last was also provoked by camphor monopoly which was introduced by Japanese government in Taiwan in 1899 and Japan in 1903. As a result of this monopoly the camphor prices almost doubled within the following seven years [1].

These demands stimulated the researches on production of synthetic camphor from accessible starting chemicals. For that reason, before the World War I in Europe and United States, a number of synthetic methods were worked out based on pinenes - one of main constituents of turpentine. The turpentine from pine which grows in North Europe (*Pinus silvestris*) contains 45-70% of α -

pinene and 2-9% of β -pinene (**Scheme 1**, compounds III and VIII, respectively). Both pinenes could be used in camphor production.

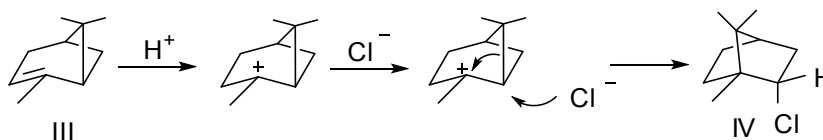
Being afraid the concurrence of synthetic camphor, Japan significantly reduced the camphor prices. This made the synthetic camphor noncompetitive and led to the closure of camphor production facilities. Nevertheless the Schering Company in Germany produced about 600 t a year of camphor before World War I and up to 2000 t a year before World War II.

Due to vast investigations in camphor synthesis and technology, a new method of camphor production was proposed in the 1930s. This method, together with earlier elaborated synthetic route, is given on the **Scheme 1** [1].



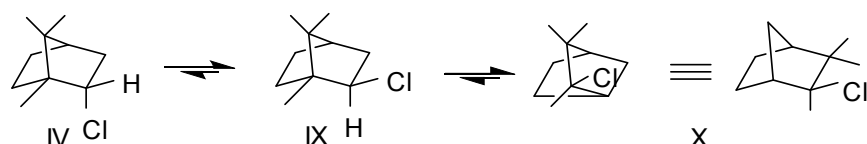
Scheme 1. General directions of camphor synthesis

The "classical syntheses" of the camphor comprises several stages; the first of them is preparation of bornyl chloride (IV) by the action of dry hydrogen chloride on α -pinene (III). The first step of this reaction is electrophilic addition of hydrogen ion followed by Wagner-Meerwein rearrangement (**Scheme 2**) [3].



Scheme 2. HCl addition to α -pinene

The next step of the "classical synthesis" includes the treatment of bornyl chloride (IV) with a base to eliminate HCl. Bornyl chloride eliminates HCl very slowly but in reaction mixture it exists in equilibrium with isobornyl chloride (IX) and 3-chloro-2,2,3-trimethylbicyclo[2.2.1]heptane (camphene hydrochloride) (X) (**Scheme 3**).



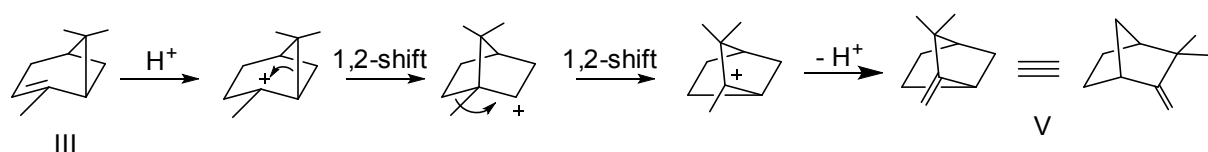
Scheme 3. Mutual transformations of bornyl chloride (IV), isobornyl chloride (IX) and 3-chloro-2,2,3-trimethylbicyclo[2.2.1]heptane (X)

3-Chloro-2,2,3-trimethylbicyclo[2.2.1]heptane (X) reacts with bases very quickly with formation of camphene (V). All these synthetic transformations from α -pinene to camphene are usually accompanied by formation of a number of bicyclic and monocyclic isomers that finally lead to admixture of isofenchone and other products which are very difficult to separate from target camphene.

These drawbacks, together with large amount of nonrecyclable byproducts, stimulated the other investigations of direct transformation of α -pinene to camphene. As early as 1910 it was found by Montland that turpentine could be converted to camphene by catalytic action of kaolin, silica or "Fuller's earth" [4].

A little later in 1915 a Russian chemist L. G. Gurvich reported the spontaneous formation of some amounts of camphene (V) when he treats pinene with specially dehydrated clay called floridine (Fuller's earth) [5]. The reaction was accompanied by a strong heating of the reaction vessel. The low yield of V was probably due to the subsequent polymerization of camphene, and that did not allow a practical implementation of the method within the next almost 15 years.

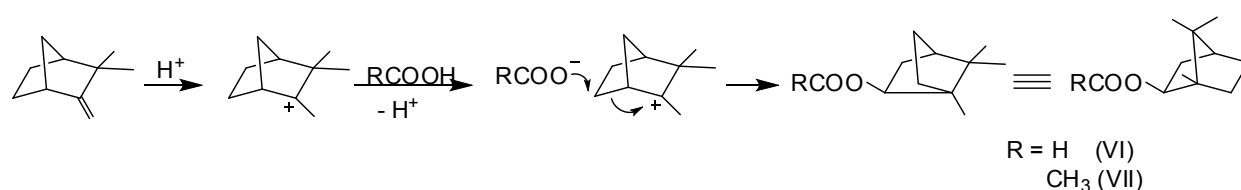
In United States in 1933 Du Pont has started a commercial production of camphor from pinene and the plant has reached annual capacity of 4000 t in 1947 [4]. Since 1931 a vast number of investigations on camphene synthesis by isomerization of α -pinene were performed in Soviet Union by Tishchenko and Rudakov which were summarized in their publication [6]. At that time α -pinene was available in the sufficient amounts because of low labor costs in the turpentine industry. Tishchenko and Rudakov have thoroughly studied a number of catalysts and various reaction conditions. The key point of isomerization synthesis is direct transformation of α -pinene (III) to camphene (V) which is also considered as a Wagner-Meerwein rearrangement (**Scheme 4**).



Scheme 4. Isomerization of α -pinene to camphene

In their synthesis Tishchenko and Rudakov used natural clay as a catalyst subjected to activation by heating with 10% of hydrochloric acid [5]. Later, Shering Co proposed the application of titanium dioxide (TiO_2) as a catalyst, which increases the yield of camphene up to 85% in comparison with 55-62% for activated clay.

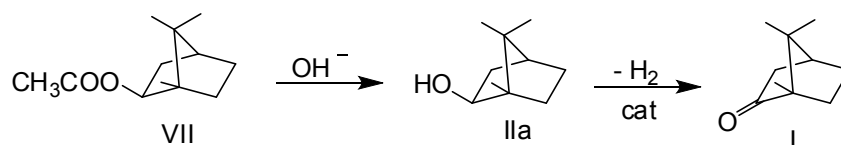
In both "classical" and isomerization pathways of camphor synthesis resulting camphene in the next step subjected to action of formic or acetic acid with formation of corresponding esters: isobornyl formate (VI) and isobornyl acetate (VII). At that time direct hydration of camphene to isborneol (II) did not receive a practical application [1]. Addition of organic acids to camphene proceeds under action of acidic catalyst (usually H_2SO_4) and accompanied by rearrangement (**Scheme 5**).



Scheme 5. Synthesis of isobornyl acetate from camphene

Isobornyl acetate (VII) is an important constituent of many essential oils, for example from needles of Siberian fir (40-45%), and its production seems more useful because isobornyl acetate possess a pleasant odor and could be used as a flavoring agent.

The next step of camphor synthesis is hydrolysis of isobornyl acetate with aqueous solution of sodium hydroxide. Then resulting isoborneol (IIa) subjected to dehydrogenation under catalysts and target camphor is obtained with a rather high yield (about 90% for both steps) (**Scheme 6**).



Scheme 6. Isobornyl acetate hydrolysis followed by dehydration to camphor

Further purification of camphor by crystallization gives a commercial grade product.

The present state of synthetic camphor production is summarized by Zhao and Bi [7]. More than 30000 t of camphor is produced annually mainly in China and India. It is noted that synthetic camphor is exported worldwide at an average price of 3500 USD/t (2008). Traditional methods through esterification of camphene followed by hydrolysis of isobornyl acetate still remains the principal pathway for camphor production. Nevertheless the direct hydration of camphene with formation of isoborneol still constitutes a significant part of it.

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